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Iron-titanium oxide minerals in layered gabbros of the Skaergaard intrusion, East Greenland

Part I. Chemistry and ore-microscopy

E. A. Vincent

Department of Geology and Mineralogy, University Museum, Oxford,

and R. Phillips

Department of Geology, Durham Colleges in the University of Durham.

(*Received* 8 *February* 1954)

ABSTRACT

The microscopic characters and chemical compositions of coexisting magnetites and ilmenites in a suite of differentiated gabbros are discussed. Textures of the minerals suggest that some discrete crystals of ilmenite owe their origin to complete exsolution from an originally homogeneous high-temperature solid solution. The magnetites contain exsolution bodies of ilmenite and sometimes of ulvöspinel, Fe_2TiO_4, those of rocks rich in opaque oxides carrying much more ulvöspinel than those of average rocks at the same horizons in the intrusion; leading to the conclusion that the magnetite compositions are largely determined by oxidation-reduction equilibria between ferrous and ferric oxides and oxygen in the crystallizing magma.

The variation in contents of Mg, Co, Mn, Zn, Cu, Al, Cr, and V in both magnetites and ilmenites is discussed. In the magnetites these vary much less than FeO, Fe_2O_3, and TiO_2 between melanocratic and average bands at the same horizon, and reflect both their ease of entry into the minerals and their availability in the magma at each stage.

1. Introduction and Previous Work

Although much has been written about the iron-titanium oxide minerals in igneous rocks, no attempt appears to have been made to examine coexisting magnetite and ilmenite in a well-defined suite of basic rocks. For the purpose of such a detailed study, magnetites and ilmenites have been separated from rocks of the unrivalled genetic suite of the Skaergaard intrusion, described by Wager and Deer (1939).

The general microscopic characters of the opaque minerals of igneous rocks have recently been summarized by Ramdohr (1950). Descriptions and chemical analyses have been given of many opaque minerals in rocks of the Bushveld complex of South Africa (Schwellnus and Willemse, 1943; Frankel and Grainger, 1941; Strauss, 1947); and there is useful information on Scandinavian examples of magmatic iron-ore minerals (Foslie, 1928; Mogensen, 1946; Landergren, 1948; Hjelmqvist, 1950), but all these deal rather with isolated rocks than with established petrogenetic series, and interest is largely focused upon their economic value.

The second-named author has carried out the microscopic examination of the Skaergaard minerals in reflected light, and is mainly responsible for section 3 of this paper. The first-named author has made the mineral separations and chemical analyses, and is responsible for the remainder of the paper.

The magnetic properties of the analyzed minerals have been investigated by Professor R. Chevallier and Mlle. S. Mathieu, of the University of Nancy, and it is intended to present an account of these as a second part of this paper.

2. Material Investigated

Opaque iron-titanium oxide minerals first appear as a primary precipitate in the layered series rather high in the hypersthene-olivine-gabbros (Wager and Deer, 1939, pp. 228–230) and eight samples have been investigated from the main horizons above this (Table 1), the rocks representing successively lower crystallization temperatures. The modal proportions of the various minerals given in Table I must be regarded as approximate only, since the area available for measurement on a polished specimen is limited, and the rocks generally show

Table 1. *Rocks of the layered series from which iron-titanium oxide minerals have been separated*

Horizon	*Estimated height in layered series (metres)*	*Rock No.† E.G.*	*Volume percentage**				*Remarks*
			Silicates	*Magnetite*	*Ilmenite*	*Sulphides*	
Fayalite-ferrogabbro	2470	4142	92·6	1·2	4·7	1·5	"Purple band," average material
	2375	1974	94·7	5·1	—	0·2	"Purple band," low
Ferrohortonolite-ferrogabbro	2050	4147	91·3	2·8	5·9	—	
Hortonolite-ferrogabbro	1730	2574	92·1	1·8	6·1	—	Approx. average material
		2569	72·5	21·4	5·8	0·3	Band very rich in opaque minerals
Middle gabbro (olivine-free)	1150	3661	86·5	7·3	6·2	—	
Hypersthene-olivine-gabbro	700	2307	88·3	6·6	5·1	—	Approx. average material
		2308	49·9	36·3	13·8	—	Band very rich in opaque minerals

* Determined by the point-counting technique of Chayes (1949).

† Numbers refer to the collection of East Greenland rocks housed in the Department of Geology and Mineralogy, Oxford.

igneous lamination so that measurement of any particular specimen may give a misleading idea of the average proportions of minerals in the rock. This last factor probably has little effect upon the measurement of the ratios of magnetite to ilmenite.

In all these rocks (with the exception of the fayalite-ferrogabbro 1974), ilmenite occurs as discrete crystals of sufficient size to be separable from the associated magnetite, and also as exsolution lamellae enclosed within the latter mineral. The

magnetites, therefore, are not homogeneous crystals, but are the results of unmixing of solid solutions. Such material is commonly termed "titanomagnetite," a name which is taken to cover all titaniferous magnetites, whether in homogeneous, rapidly cooled, or in heterogeneous, slowly cooled crystals. Titanomagnetite is defined in the 7th edition of DANA's "System of Mineralogy" as a homogeneous variety of magnetite containing up to $7\frac{1}{2}\%$ TiO_2, and it would seem proper not to extend the meaning to cover magnetite carrying exsolution bodies of ilmenite, to which the term "ilmenomagnetite" (BUDDINGTON, 1953, private communication) may perhaps better be applied. For the sake of simplicity and ease of reference the name magnetite is used in this paper to cover all the strongly ferromagnetic materials in these rocks, despite their heterogeneity.

Some of the magnetites also contain appreciable quantities of the iron-titanium spinel Fe_2TiO_4, which, following MOGENSEN (1943) and RAMDOHR (1953a,b) has been called "ulvöspinel" when present as a separate exsolved phase. Solid solution series have been referred to by the chemical formulae of their end-members.

3. MICROSCOPIC EXAMINATION OF THE MINERALS

(a) *Descriptions of polished specimens*

The following descriptions are arranged in ascending order in the layered series.

The ore-rich hypersthene-olivine-gabbro (2308) contains groups of individual $\frac{1}{2}$–$1\frac{1}{2}$ mm grains of ilmenite and magnetite, as shown in Plate 1A, in mutual boundary texture with the transparent minerals. The ilmenite is strongly anisotropic and pleochroic, and shows very fine anisotropic lamellae, 1μ in width, parallel to (0001), which are thought to consist mainly of magnetite with a little $FeTiO_3$ in solid solution, together with some transparent spinel.

The magnetite is brownish-white in colour, rather similar to the colour in air of the extraordinary ray of ilmenite. At a magnification of 400 diameters the mineral is seen to contain two constituents intimately intergrown on a minute scale.[1] One of these, most probably ulvöspinel Fe_2TiO_4, is darker brown in colour, the other, magnetite Fe_3O_4, lighter brown than the overall colour effect. Under oil immersion (Plate 1B) the intergrowth of the two phases has the appearance of a closely-woven piece of cloth (cf. MOGENSEN, 1946, Fig. 4; RAMDOHR, 1953b, Fig. 14; HJELMQVIST, 1950, Fig. 30). Careful examination shows a series of roughly parallel needles of the darker brown ulvöspinel (cf. RAMDOHR, 1950, p. 663), which are not always quite straight, approximately $\frac{1}{4}\mu$ in width and up to 5μ long. Locally the texture is more clearly developed, as shown in the sketch, Fig. 1.

X-ray powder photographs of magnetite drilled from the polished specimens prove the presence of the two spinel phases, while chemical analysis (Table 2, analysis 2) suggests that they are present in roughly equal amounts.

Owing to slight differences in hardness, one constituent will tend on polishing to stand slightly in relief above the other, and oblique incidence of light on the bevelled edges of the harder material is probably the cause of a weak false anisotropy observed in the grains.

The magnetite is not attacked by the normal etch reagents of SHORT (1940), but slowly turns brown with concentrated hydrochloric acid. Momentary immersion (about 2 seconds) of the whole specimen in 40% hydrofluoric acid, followed immediately by washing in running water, revealed on most of the magnetite grains small euhedral, isotropic crystallites, with outlines characteristic of the cubic system (Plate 1C). The rhomb-shaped crystallites have a maximum diagonal length of about 30μ. The crystallites are themselves slightly etched, but less so than the surrounding intergrowth texture, which in many cases is seen to continue across

[1] These fine structures in the magnetite of rock 2308 had not been discerned using the ore-microscope, or with X-rays, at the time the footnote on p. 156 of WAGER and MITCHELL's paper (1951) was written. It was there stated that this magnetite appeared to be free from exsolution lamellae.

them, while the Kalb light line test shows that they stand in relief above the general surface level, and are not therefore etching pits. Since the crystallites are less etched than the rest of the magnetite host, and are cubic in form, they also are thought to be ulvöspinel.

Despite careful search, the crystallites could not be detected on unetched material, and although they are partly of primary growth (being cut by fine transparent mineral veinlets), they are also developed as artefacts along undoubted polishing scratches.

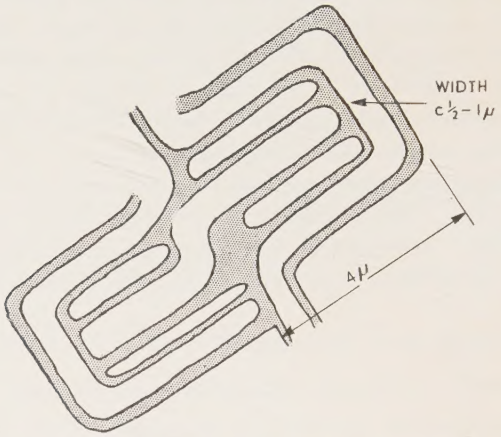


Fig. 1. Detail of cloth-texture in magnetite 2308.
Dotted areas are ulvöspinel, white magnetite.

Under high power (× 400) two of the magnetite grains in the polished specimen of 2308 show a series of unetched, or slightly etched, isotropic lamellae ½–1μ in width, in triangular texture, with heavily etched inter-lamellar spaces. At one point a small area of cloth-like magnetite-ulvöspinel intergrowth containing only a few of these lamellae is seen passing into the triangular texture. This kind of relationship, better developed in the magnetites of the rocks 2307 and 3661, described below, seems to trace a connexion between the cloth-like exsolution of ulvöspinel and the triangular pattern assumed by the exsolved ilmenite in most of the magnetites.

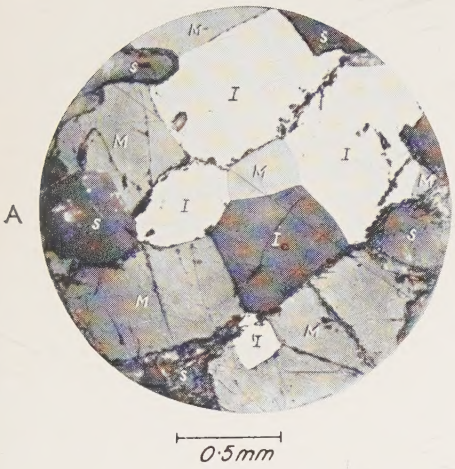
Some few grains also show fine lamellae and rhomb-shaped crystals, 1–2μ in size, of a transparent mineral, believed to be a spinel exsolved from the magnetite. Their distribution near grain boundaries veined by transparent minerals seems to indicate some local reaction between magnetite and the silicate magma. A similar development on a larger scale in magnetite from the Bushveld complex is described by Strauss (1947).

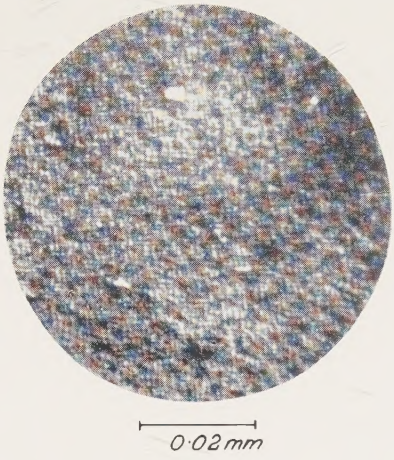
Fine veinlets, 1μ wide, of transparent minerals, not visible before etching, cut the magnetite and its contained crystallites of ulvöspinel. These have a narrow border, about 8μ wide, of acicular ulvöspinel, locally with larger needles up to 40μ in length. Most of these needles have a core of ilmenite; others are mainly ilmenite with but a narrow sheath of ulvöspinel; while some are entirely composed of ilmenite. They are usually arranged with their long axis perpendicular to the vein margin. There are also a few ilmenite lenticles up to 8μ in length and 1μ wide situated within the magnetite grains.

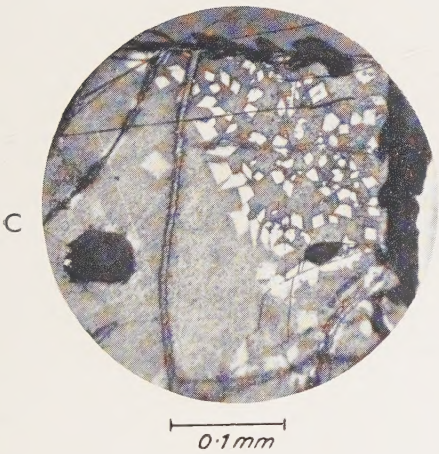
In the average hypersthene-olivine-gabbro (2307) there are groups up to 2 mm across of associated ilmenite and magnetite grains, and also isolated grains of the two minerals varying from ¼ to 1 mm in size.

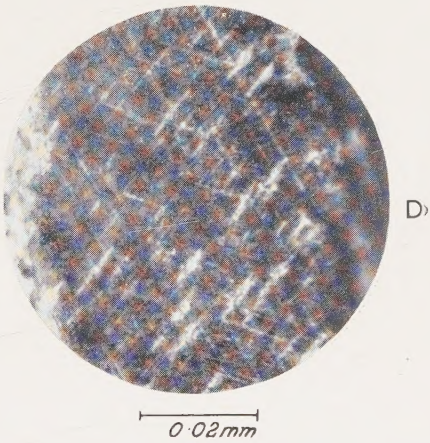
The ilmenite is similar to that of 2308, with perhaps a more marked tendency to be elongated parallel to (0001), and showing only slight pleochroism.

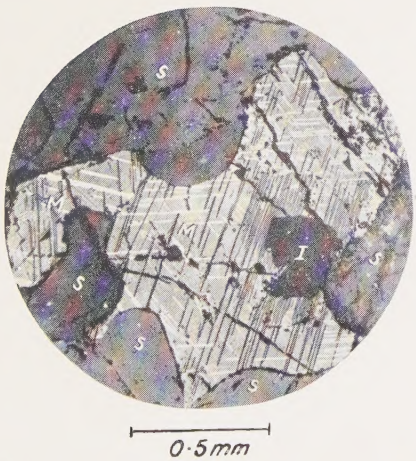
The magnetite does not show the marked brown colour of 2308; it is whitish, but between crossed polars again shows a weak anisotropy. Cloth-like intergrowth of magnetite and ulvöspinel is visible locally at 400 diameters magnification. After momentary etching with 40% hydrofluoric acid crystallites are rarely seen, but all the grains show lamellae of ulvöspinel in the fine











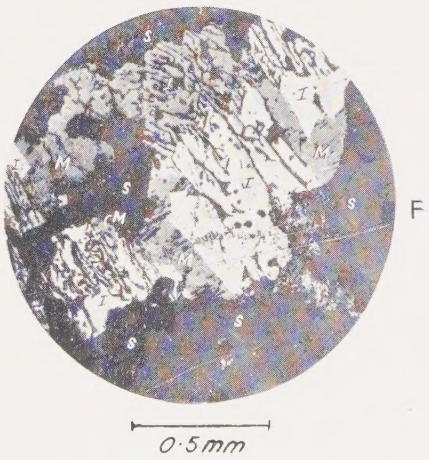


PLATE 7

For detailed explanation see back plate

EXPLANATION OF PLATE I

A. Photomicrograph of a cluster of opaque mineral grains in ore-rich hypersthene-olivine-gabbro, 2308, showing curvilinear sealed boundaries between magnetite and ilmenite grains. M = magnetite; I = ilmenite; S = silicates.
Reflected light; polars 5° from crossed position; magnification × 27.
(From WAGER and MITCHELL, 1951, Fig. 4.)

B. Photomicrograph of a crystal of magnetite in rock 2308, showing cloth-like intergrowth between magnetite and ulvöspinel. Specimen etched with HF, Reflected light; oil immersion; magnification × 770.

C. Photomicrograph of another crystal of magnetite in rock 2308, after etching with HF, showing light-toned crystallites, probably of ulvöspinel, revealed in the darker-toned magnetite. In the top half of the field veinlets of transparent silicates are seen to cut the crystallites.
Reflected light; magnification × 150.

D. Photomicrograph of a magnetite crystal in rock 2307 showing cloth-like intergrowth of ulvöspinel and magnetite passing over into lamellae of ulvöspinel in triangular texture. Specimen etched with HF.
Reflected light; magnification × 770.

E. Photomicrograph of magnetite in the ore-rich hortonolite-ferrogabbro 2569, showing well-developed exsolution lamellae of ilmenite in triangular texture. To the right of the field the lamellae are densely clustered around a small grain of ilmenite which has itself probably been formed by early exsolution from the magnetite. M = magnetite; I = ilmenite; S = silicates.
Reflected light; polars 5° from crossed position; magnification × 36.
(From WAGER and MITCHELL, 1951, Fig. 4.)

F. Photomicrograph of ores in the fayalite-ferrogabbro 4142. Note the corrosion and invasion of the ilmenite by magmatic solutions. M = magnetite with exsolution lamellae; I = ilmenite; S = silicates.
Reflected light; polars 8° from crossed position; magnification × 36.

triangular texture developed to a much smaller extent in 2308 (Plate 1D). Parts of these lamellae have in some cases changed over to ilmenite. Numerous small exsolution lamellae of ilmenite are also visible under high power.

In the middle gabbro (3661) individual grains of magnetite and ilmenite up to $1\frac{1}{2}$ mm in size occur in aggregates up to 3 mm across, similar in general appearance to those in the hypersthene-olivine-gabbro 2308.

The ilmenite is similar to that of 2308, except that the fine lamellae can only be seen under high power ($\times$ 400).

The magnetite shows a few ilmenite lamellae under low power, but under high power many minute ilmenite rods in triangular texture are seen. Etching with hydrofluoric acid shows the only ulvöspinel observed to be in fine triangular texture set in a matrix of heavily-etched magnetite, the minute ilmenite rods having developed as part of this texture.

The ore-rich hortonolite-ferrogabbro (2569) carries composite elongated patches of opaque oxides up to 1 cm in length composed of magnetite and ilmenite grains up to 3 mm long and $\frac{1}{2}$–2 mm wide.

The magnetite contains long ilmenite lamellae in triangular texture, and some small ilmenite grains (Plate 1E). At 400 diameters magnification the very abundant ilmenite lamellae are seen to range in size down to the limit of visibility. Here and there in the inter-lamellar spaces very fine isotropic lamellae are seen, believed to be ulvöspinel, while some grains show only a few ilmenite lamellae set in a cloth-textured intergrowth of magnetite and ulvöspinel.

The opaque oxides of the average hortonolite-ferrogabbro (2574) occur in patches up to 2 mm in maximum dimension, and even casual inspection shows that ilmenite is present in excess of magnetite. Much of the ilmenite occurs as separate elongated granular aggregates, but some grains are enclosed in the magnetite, all of which also has closely-spaced lamellae of ilmenite in triangular texture.

Etching of the magnetite with hydrofluoric acid has little effect: the surface is slightly discoloured, and the ilmenite lamellae stand out in relief.

The maximum grain size of the opaque oxides in the ferrohortonolite-ferrogabbro (4147) is $1\frac{1}{2}$ mm. Ilmenite occurs without associated magnetite in grains of various sizes; also as large and small grains associated with magnetite, which in addition always contains some large ilmenite lamellae 10–20μ in width. This magnetite has a weak anisotropy with slight dispersion, which is found to be due to a further series of minute included rods and irregular elongated bodies of ilmenite, from sizes just visible at 400 diameters magnification down to the limit of visibility in oil ($\times$ 950). No ulvöspinel has been detected, although the chemical analysis suggests that about 9% may be present.

The fayalite-ferrogabbro (1974) carries only magnetite grains, from $\frac{1}{4}$–1 mm in size, with lamellae of ilmenite, locally in seriate texture. There are no separate grains of ilmenite, but the lamellae enclosed in the magnetite are much more numerous than in any other rock examined and are markedly pleochroic. Near the grain boundaries the lamellae are commonly invaded by transparent silicates penetrating along (0001) planes to give a micro-texture similar to that developed on a larger scale in the rock 4142.

The fayalite-ferrogabbro (4142), the highest in this genetic series, carries magnetite grains up to 1 mm in size containing abundant ilmenite lamellae and ilmenite grains of various sizes. Ilmenite also occurs as large grains without associated magnetite, and in many cases these have grown around idiomorphic apatite crystals. The ilmenite lamellae and grains both show the textural relationship with transparent minerals illustrated in Plate 1F. Some replacement of ilmenite by transparent silicates appears to have taken place along (0001) planes, leading eventually to a group of isolated residual finger-shaped areas.

(b) *Interpretation of the textural relationships*

(i) *Evidence of exsolution.*

The granular magnetite-ilmenite aggregates found in the earlier rocks (e.g. the hypersthene-olivine-gabbro 2308, Plate 1A) could result from either of two processes: the aggregation of separately precipitated grains, as in the synneusis

texture of VOGT (1921), or by the unmixing of an originally homogeneous Fe_3O_4—$FeTiO_3$—Fe_2TiO_4 solid solution into large crystal units.

The observed relationships suggest that the second process may be responsible.[1] If this were a synneusis texture, we would expect to find chain-like aggregates of idiomorphic grains, some of them consisting of ilmenite without magnetite, and vice versa. This is not seen, and although plane faces are developed on some of the grains, they do not generally appear to be the normal low-index faces of idiomorphic magnetite and ilmenite. The outer margins of the aggregates show mutual boundary texture with the transparent minerals, due mainly to contemporaneous precipitation, although some reaction between the oxide margins and the magmatic solutions has occurred. If the oxide grains had been separately precipitated, all the grain faces would be expected to show similar features. In fact, the boundary between magnetite and ilmenite is usually of a type best described as a sealed boundary—an extremely sharp line of junction, with no other material included between the two, and usually smooth and gently curving.

It has been shown (SMITH, 1952) that two different lattices may unite without any discontinuity at the interface, provided that the junction surface is gently curving. Such a relationship could well be a consequence of unmixing giving two minerals from a single solid solution, but it is unlikely to result from the aggregation of separately precipitated grains. Occasional irregular projections of magnetite into ilmenite, and vice versa, are seen, which are not easily explained by the hypothesis of separate precipitation but are to be expected as a result of unmixing. Granular aggregates of magnetite and ilmenite similar to these observed in the lower rocks of the Skaergaard layered series have been described by EDWARDS (1938), and interpreted by him also as due to complete unmixing of a solid solution.

Various stages in such an unmixing process can be followed in the higher rocks of the series. The hypothesis also explains satisfactorily why magnetite and ilmenite both first appear as primary precipitate minerals at the same time.

Despite fairly complete unmixing into separate crystals in the earlier rocks, both the phases formed continued to exsolve material on further cooling, but, probably because of restricted solid diffusion at lower temperatures, this material has assumed the form of exsolution lamellae. The series of fine lamellae noted in the ilmenites of 2307, 2308, and 3661 show that this exsolved mineral itself carried only minor amounts of other material in solid solution; the magnetites of the earlier rocks, on the other hand, probably because of the reduced state of the Skaergaard magma, carried appreciable amounts of Fe_2TiO_4 in solid solution.

The observed relationships in the ore-rich hortonolite-ferrogabbro 2569 appear to be due to incomplete separation of ilmenite and magnetite as discrete crystal units from an originally homogeneous solid solution. The ilmenite which presumably has separated at high temperatures forms fair-sized grains near the boundary of the magnetite; while the exsolution lamellae of ilmenite have presumably formed at lower temperatures, when solid diffusion was more limited (Plate 1E).

[1] This textural feature was remarked upon by WAGER and MITCHELL (1951, p. 153) and interpreted by them as due to weak magnetic attraction between the grains at high temperature. Professor WAGER now concurs in the view that it is more likely to be an exsolution texture.

In the average hortonolite-ferrogabbro 2574 there is for the first time an excess of ilmenite over magnetite, and some at least of the separate ilmenite grains appear on textural grounds to have been precipitated as such from the magma, in addition to the homogeneous high-temperature solid solution which later exsolved ilmenite.

If the bulk compositions of the opaque oxide content of the various rocks are calculated from chemical and modal analyses, the rocks 2308, 3661, and 2569 are

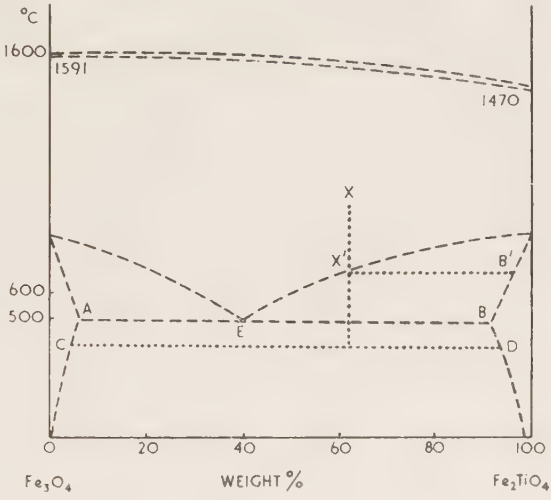


Fig. 2. Tentative phase relationships in the system Fe_3O_4—Fe_2TiO_4.

seen to have approximately the same ratios of magnetite to ilmenite. The different extent of exsolution observed in these rocks, from complete unmixing in 2308 to partial unmixing in 2569, may thus represent the effect of falling temperature.

In the higher rocks of the series, consideration of the exsolution processes is complicated by the presence of separately precipitated ilmenite: it also seems likely that the accompanying high-temperature solid solution was nearer ilmenite than magnetite in original composition.

(ii) *Tentative phase relationships in the system* Fe_3O_4—Fe_2TiO_4.

Fe_3O_4 and Fe_2TiO_4 are known from laboratory experiments to form solid solutions at high temperatures (Pouillard and Michel, 1949; Chevallier and Girard, 1950), the ulvöspinel having the inverse spinel structure. Such solid solutions may persist as homogeneous crystals in fine-grained, rapidly cooled rocks, while unmixing of the two phases can be anticipated in slowly cooled, deep-seated rocks.

Although there is no published information on the sub-solidus relationships of magnetite and ulvöspinel, the textures described between these two minerals could be explained if the phase diagram were of the form shown in Fig. 2.

A homogeneous solid represented by the point X on cooling to X′ will form crystals of composition B′. Further cooling would cause the composition of the crystals to change towards B, whilst the remaining solid would change towards E, where a eutectoid intergrowth of A and

B would be formed. The cloth-texture described in some of the magnetites is believed to be such an intergrowth, and its appearance as shown in Fig. 1 is similar to certain metallurgical examples of eutectoids.

On further cooling, both the A and B of the eutectoid and the B crystals are made over to solid solutions C and D, whose composition changes with decreasing temperature.

The magnetite described by Mogensen (1946) contained 52% Fe_2TiO_4, and became homogeneous on heating to 600°C. The exsolution curve in Fig. 2 is therefore drawn to pass through 600°C at this composition, although this temperature may not be the minimum required for homogenization. The Skaergaard magnetite 2308 contains 43% Fe_2TiO_4 (Table 2) and shows some primary crystallites of ulvöspinel. The eutectoid composition is therefore provisionally placed at about 40% Fe_2TiO_4 and at a temperature of about 500°C.

If we now consider the genesis of the opaque oxides in the rock 2308, it seems likely that ilmenite was exsolved from the titaniferous magnetite fairly completely, to give large crystal units. On further cooling, the remaining homogeneous titaniferous magnetite formed a mixture of ulvöspinel-rich crystals B in eutectoid E. Owing to the low temperature of the eutectoid solid diffusion was limited, and this state was frozen before equilibrium had been attained, except in the case of a few grains where these phases were made over to an oriented intergrowth of C and D type solid solutions in triangular texture. Those crystallites of ulvöspinel which are distributed along polishing scratches may owe their origin to repolishing of the specimen, when local overheating could raise the temperature into the region represented by X′, causing growth of B-B′ type crystallites of ulvöspinel, which were again frozen on fairly rapid cooling. The temperature produced locally on polishing is limited only by the melting point of the material, as has been shown by experiment (Bowden, 1947), and the formation of a thin layer due to surface flow—the Beilby layer—has long been known. With rising temperature crystal growth in this layer would increase rapidly, since the increase of the rate of solid diffusion with temperature is of exponential form.

In the case of the average rock 2307 from the same horizon in the intrusion, the majority of the magnetite grains show the fine triangular texture of ulvöspinel in magnetite, cloth-texture with crystallites being comparatively rare. It is possible in this case that temperatures allowing solid diffusion were maintained long enough for establishment of the C-D type of equilibrium on the diagram.

The ilmenite needles described in the magnetite of the ore-rich band 2308 are believed to have developed by oxidation of ulvöspinel, while in the average rock 2307 parts of the ulvöspinel lamellae in triangular texture have similarly changed to ilmenite. A more advanced stage of this oxidation process is perhaps illustrated by the magnetite of the middle gabbro 3661, where the majority of the ulvöspinel lamellae have been oxidized to ilmenite.

4. The Chemical Analyses

(a) *Methods of separation and analysis*

Magnetite was extracted from the finely-crushed rock powders by means of a weak permanent horseshoe magnet. The bulk of the contaminating silicate grains were removed by repeated centrifuging in Clerici solution and, after crushing to an average grain size of 0·05 mm and smaller, the samples were finally purified by passing them several times through a Frantz magnetic separator, utilizing the residual magnetism of the pole-pieces, the current being turned off.

Ilmenite was then concentrated by centrifuging the magnetite-free rock powders in warm, saturated, Clerici solution, the samples being finally purified with the magnetic separator, and in a few cases by hand-picking.

The analyzed magnetites are at least 98–99 per cent pure, as estimated from grain counts, and in most cases better. The purity is a little less than this in the cases of the magnetites 2307 and 2574, which were originally intended only for partial analysis. All the ilmenites are at least 99 per cent pure, and probably most samples are purer than this.

The opaque minerals are often traversed by very narrow transparent veinlets, so that complete elimination of silicates from the analyzed samples is not to be expected. The analyses themselves, however, indicate that the contamination is small.

The amounts of the final purified concentrates of magnetite and ilmenite from each rock weighed generally between 0·1 and 0·5 g and the analyses were carried out on a semi-micro scale, all weighings being made to the fifth decimal place. A considerable time was spent in trying out available methods for the determination of the various constituents and, although none of them is new, the writer feels that it might be useful to others working on these minerals to state briefly the procedures which were finally adopted.

Ferrous iron—15–20 mg portions were weighed into 5 ml platinum crucibles, moistened with distilled water, and a mixture of 1 part boiled and cooled distilled water, 1 part sulphuric acid and 2 parts hydrofluoric acid added. The covered crucible was then heated for 5 minutes at 160°C in an electrically heated aluminium heating block, at the end of which time it was plunged into a mixture of 40 ml saturated boric acid and 5 ml 50% sulphuric acid and the solution titrated with N/50 ceric sulphate from a micro-burette, using *o*-phenanthroline-ferrous sulphate complex as indicator. This method gave consistent results with very sharp end-points in the titrations, and all the minerals were completely decomposed. Control experiments with weighed portions of ferrous ammonium sulphate showed that there was no oxidation of ferrous iron under these conditions. Determinations were made in duplicate or triplicate, and the results corrected where necessary for the presence of vanadium.

Total iron—15–20 mg portions were very finely ground and fused in small silica crucibles with 0·1 g of potassium pyrosulphate. The cooled melts were dissolved in N/1 hydrochloric acid, the solutions passed through a silver reductor, as described by Miller and Chalmers (1952), and titrated in an atmosphere of carbon dioxide with N/50 ceric sulphate in the presence of sulphuric acid and using *o*-phenanthroline-ferrous sulphate complex as indicator. This method has the great advantage that there is no interference from titanium or vanadium in the determination of iron. Duplicate determinations were made.

Silicon, aluminium, chromium, and vanadium—About 50 mg of sample was decomposed in a platinum crucible by sintering with 0·2 g of sodium peroxide in the electric furnace at 480°C (Rafter, 1950). The sintered mass was leached with water in a small platinum dish, the mixture boiled for 10 minutes to decompose peroxides and to coagulate the residue, filtered through a very small toughened filter-paper into a 25 ml volumetric flask, the filtrate neutralized with hydrochloric acid and made up to volume.

SiO_2—A 5 ml aliquot of this solution was used for the colorimetric[1] determination of silica by the molybdenum blue method using the procedure described by Shapiro and Brannock (1952). This method yielded highly reproducible results and is vastly preferable to any attempt at isolating small amounts of silica by evaporation with acids, especially in the presence of much titanium. Carefully controlled blank determinations were made. It is possible that a trace of silica may be derived from the agate mortar used in the fine grinding of the sample, but tests showed that the amount so derived must be small (not exceeding the equivalent of 0·05% SiO_2 on the weights of sample used).

Al_2O_3—A second 5 ml aliquot was used for the colorimetric determination of aluminium, using the aurintricarboxylic acid method as described by Sandell (1950, pp. 156–157). Since a small trace of iron nearly always accompanies aluminium into the filtrate from the sodium peroxide decomposition, and also forms a coloured lake with the reagent used, it was necessary

[1] All colorimetric determinations were made with the latest model Hilger "Spekker" photoelectric absorptiometer.

to determine colorimetrically the amount of iron present and its effect upon the aluminium determination, and make the necessary small correction. Imperfect though this method is, it is far superior to the estimation of small amounts of aluminium by difference in a bulk ammonia precipitate.

Cr_2O_3—A third aliquot was treated with 6N sulphuric acid and diphenylcarbazide for the colorimetric determination of chromium (Sandell, 1950, pp. 265–266).

V_2O_3—A fourth aliquot was used for the colorimetric determination of vanadium, using the phosphoric acid–sodium tungstate method (Sandell, 1950, pp. 607–609).

Titanium, calcium, and magnesium—40–100 mg of sample were decomposed with sodium peroxide, the sintered mass dissolved in dilute hydrochloric acid, and the solution boiled to expel chlorine and decompose peroxides. A double ammonia precipitation was carried out, the final precipitate being dissolved in hydrochloric acid and used directly for the gravimetric determination of *titanium* by the phenazone-tannic acid method (Moser, Neumayer, and Winter, 1930). This method gave excellent results, and the bulky precipitate first obtained is very satisfactory when dealing with small weights of sample.

Calcium was determined in the filtrate from the ammonia precipitate, by double precipitation of the oxalate, the final precipitation being made in a micro-beaker. The oxalate was filtered through a porous porcelain filter-stick, ignited to the carbonate at 500°C in the electric furnace, and weighed.

Magnesium was determined as 8-hydroxyquinolate in the filtrate from the calcium, after destruction of ammonium salts. The weighed precipitate was removed from the filter-tube, ignited to MgO in a small crucible, dissolved in sulphuric acid, and the contained manganese determined colorimetrically, the necessary correction being applied to the figure for MgO.

Manganese—Small samples of the minerals were fused with potassium pyrosulphate, the cooled melts dissolved in dilute sulphuric acid, and manganese determined colorimetrically as permanganate.

Phosphorus—Small samples were again fused with pyrosulphate, and the hydrochloric acid solutions treated as described by Chalmers (1953) for the colorimetric determination of phosphorus in the presence of silica by a molybdenum blue method.

Copper, zinc, and lead—Further portions of the minerals were fused with potassium pyrosulphate, and the cooled melts dissolved in dilute hydrochloric acid. The solutions were treated with ammonium citrate and ammonia, and the copper, zinc, and lead extracted with dithizone, as described by Sandell (1950, pp. 314–315). Zinc and lead were determined in the dilute acid extract from the mixed dithizonates, using the dithizone methods for their final colorimetric measurement; while copper was determined colorimetrically with sodium diethyldithiocarbamate after evaporation of the remaining copper dithizonate and its destruction with sulphuric and perchloric acids (Sandell, 1950, p. 309).

(b) *Major constituents of the magnetites, and consideration of the phases present*

The results of chemical analysis of all the magnetite samples are assembled in Table 2, together with formal recalculations. Two magnetites have been analyzed from the lowest horizon in the hypersthene-olivine-gabbros at which primary magnetite and ilmenite are found; the two rocks 2307 and 2308, used for mineral separation, are specimens of a lighter, more average band, and of an adjacent highly melanocratic band respectively (Wager and Deer, 1939, pp. 92–93). The former contains about 12% by volume of ores, while the latter carries as much as 50%.

The polished specimen and the X-ray powder photograph of 2307 show that the mineral is essentially magnetite with some exsolved ilmenite and ulvöspinel, and the recalculation of the analysis (Table 2, analysis 1) shows an excess of FeO which has been allotted to the Fe_2TiO_4 molecule. The magnetite from the adjacent melanocratic rock, 2308 (analysis 2), has a far greater excess of FeO, and on

recalculation of the analysis ulvöspinel predominates over magnetite, while there is far less ilmenite. X-ray powder photographs of the analyzed material show strong lines of the magnetite pattern which are shadowed or doubled at all but the lowest θ-values by much weaker lines of the ulvöspinel pattern.[1] The ulvöspinel lines are just visible in the film of 2307, but are not so definite as in 2308. Measurements of the films, taken in a 114·6 mm diameter camera, gave the cubic cell dimension $a = 8{\cdot}39$ Å for the magnetite and $a = 8{\cdot}48$ Å for the ulvöspinel, values which are in fair agreement with those quoted in the literature. The X-ray film and the polished specimens show that the magnetite of 2308 also contains a few per cent of exsolved ilmenite, as is also indicated by the analysis.

The analysis of the next magnetite in the series, from the middle gabbro 3661 (Table 2, analysis 3; Wager and Deer, 1939, pp. 96–99), shows clearly that here the mineral is essentially magnetite with exsolved ilmenite. The lines of both patterns appear in the X-ray film, and are fairly sharp and well-defined, in contrast to the magnetite lines in the films of 2307 and 2308 which are shadowed by the lines of the ulvöspinel pattern. Again, the excess of FeO in the analysis has been assigned to ulvöspinel (7·9%): this phase has been identified under the microscope, but it is difficult to say whether it has caused any broadening of the magnetite lines in the X-ray film.

Two examples from the hortonolite-ferrogabbro horizon (Wager and Deer, 1939, pp. 98–103) bear the same relationship to one another as do 2307 and 2308 from the hypersthene-olivine-gabbro horizon, that is, one is from an average band and the other from an adjacent melanocratic band. The magnetite from the average rock 2574 (Table 2, analysis 4) appears to be magnetite with exsolved ilmenite in the ratio of about 2 : 1. Here, no excess of FeO remains on recalculation: indeed, the analysis shows an excess of nearly 1% TiO_2 over that required to combine with the available FeO in ilmenite. Inclusions of rutile, sometimes described in such minerals, have not been found; and it must be remembered that the recalculation of the analysis is somewhat arbitrary, so that the excess of TiO_2 may not in fact be real.

The magnetite of the melanocratic band 2569 (Table 2, analysis 5) recalls that of 2308. The magnetite lines in the X-ray powder photograph are shadowed by those of ulvöspinel, but there is also much exsolved ilmenite. Recalculation of the analysis suggests that ilmenite and ulvöspinel should be present in about equal proportions.

The magnetite of the ferrohortonolite-ferrogabbro 4147 (Wager and Deer, 1939, pp. 104–107) is not very different in overall composition from that of the middle gabbro 3661, and consists predominantly of Fe_3O_4 (Table 2, analysis 6). The X-ray film shows very sharp magnetite lines, with no sign of shadowing or doubling, yet its analysis suggests that it contains about 9·5% of the Fe_2TiO_4 molecule. Measurements of its magnetic properties, to be published in Part II of this paper, indicate that only 2% of Fe_2TiO_4 remains in solid solution in this magnetite; so that the remainder must be present as ulvöspinel exsolved on such a fine scale as not to be discernible with the microscope. The absence of ulvöspinel

[1] We are indebted to Mr. E. Z. Basta, who first pointed out these ulvöspinel lines on our films.

Table 2. Chemical analyses of magnetites from the Skaergaard intrusion (Analyst: E. A. Vincent)
(In ascending order in the layered series)

Horizon:	Hypersthene-olivine-gabbro		Middle gabbro	Hortonolite-ferrogabbro		Ferro-hortonolite-ferrogabbro	Fayalite-ferrogabbro		
Analysis No.:	1	2	3	4	5	6	7	8	Fe_3O_4
Rock No.:	2307	2308 Melanocratic band	3661	2574	2569 Melanocratic band	4147	1974	4142	
Wt. %									
FeO	37·23	43·07	35·68	33·25	41·69	35·69	37·79	37·01	31·03
MgO	1·23	1·98	1·19	1·42	1·21	0·77	0·28	0·06	
MnO	0·33	0·33	0·27	0·43	0·45	0·25	1·02	0·64	
CaO	0·30	0·42	0·30	0·47	trace	0·93	0·54	0·81	
Fe_2O_3	42·14	32·27	42·95	45·33	31·26	45·86	31·20	39·58	69·97
Al_2O_3	0·90	0·78	1·16	0·87	0·91	0·67	0·43	0·41	
V_2O_3	1·59	1·74	1·61	0·32	0·40	nil	nil	nil	
Cr_2O_3	0·09	0·13	nil	nil	nil	nil	nil	nil	
TiO_2	15·40	19·28	16·28	17·16	23·74	15·08	28·09	19·68	
SiO_2	0·58	0·24	0·35	0·92	0·23	0·66	0·71	1·80	
P_2O_5	n.d.	0·03	0·02	n.d.	0·02	0·04	0·06	0·04	
H_2O	0·04	0·06	0·05	0·06	0·09	0·11	0·04	0·08	
Total	99·83	100·33	99·86	100·23	100·00	100·06	100·16	100·11	100·00
Parts per million									
Zn	1200	1200	950	850	750	1300	1700	650	
Cu	150	100	100	600	350	400	300	200	
Calculated compositions:									
Wt. %									
$CaO.SiO_2$	0·61	0·46	0·61	0·97	—	1·28	1·11	1·67	
$MgO.SiO_2$	0·43	—	0·05	0·69	0·38	—	0·22	—	
$FeO.SiO_2$	—	—	—	—	—	—	—	2·06	
$MgO.Al_2O_3$	1·25	1·08	1·60	1·21	1·27	0·94	0·60	0·21	
$FeO.Al_2O_3$	—	—	—	—	—	—	—	0·43	
$CaO.Fe_2O_3$	—	0·75	—	—	—	1·21	—	—	
$MgO.Fe_2O_3$	3·48	8·30	3·56	3·96	3·46	2·50	0·10	—	
$MnO.Fe_2O_3$	1·06	1·06	0·88	1·40	1·45	0·81	3·32	2·07	
$FeO.V_2O_3$	2·35	2·58	2·38	0·47	0·60	—	—	—	
$FeO.Cr_2O_3$	0·13	0·18	—	—	—	—	—	—	
$FeO.Fe_2O_3$	56·00	35·33	57·29	59·74	39·87	61·50	41·80	55·34	
$FeO.TiO_2$	18·13	7·14	25·55	30·80	28·48	22·23	52·48	35·49	
$2FeO.TiO_2$	16·32	43·39	7·88	—	24·40	9·49	—	2·75	
TiO_2	—	—	—	0·93	—	—	0·43	—	
	99·76	100·27	99·80	100·17	99·91	99·96	100·06	100·02	

NOTES:

1. Zinc has not been included in the summation of the analyses, since some or most of it will have accompanied magnesium in the 8-hydroxyquinoline precipitation, and no correction for this has been attempted.
2. The calculated mineral compositions are somewhat arbitrary, but an attempt has been made to redistribute the various constituents found in the analyses into possible spinel molecules, ilmenite, and silicates. They are to be regarded merely as "norms," and the sequence of recalculation follows the order in which the molecules are set out in the table. After the sesquioxides have been allotted, the remaining TiO_2 and FeO are balanced by means of a simultaneous equation between $FeTiO_3$ and Fe_2TiO_4

lines on the X-ray photograph may be due either to such an extremely fine scale of exsolution, or to its presence in insufficient quantity to give X-ray reflections.

Recalculation of the analysis (Table 2, analysis 7) of the first of the two magnetites (1974) separated from fayalite-ferrogabbros of the 'Purple Band' horizon (Wager and Deer, 1939, pp. 108–112) shows ilmenite to preponderate over magnetite, in agreement with the microscopic observations. The rock 4142, however, taken as average material from this horizon, carries some magnetite and ilmenite as discrete crystals, but mostly complex intergrowths of the two phases with inclusions of transparent silicates, and the purity of this magnetite concentrate is almost certainly less than the others. The analysis (Table 2, analysis 8) shows magnetite to preponderate over ilmenite, and possibly the presence of a little Fe_2TiO_4.

Chemical analyses of other natural magnetites containing the Fe_2TiO_4 molecule seem to be rare. The best-known example is of the magnetite mined as an ore in the dolerite of Södra Ulvön, northern Sweden, and described in detail by Mogensen (1946). Foslie (1928) suggested that the Fe_2TiO_4 molecule might enter into the constitution of the magnetite he separated from the ilmenite-norite of Storgangen, Norway, but no X-ray data were given. Hjelmqvist (1950) gives an analysis of "titanomagnetite" from Taberg in southern Sweden which again carries an excess of FeO. In this case, X-ray examination did not reveal with certainty the presence of ulvöspinel, but examination of Hjelmqvist's published photomicrograph almost certainly shows this phase exsolved in the magnetite. Vaasjoki (1947) also gives a magnetite analysis with an excess of FeO.

These various analyses are reproduced for purposes of comparison in Table 3,

Table 3. Chemical analyses of some magnetites containing excess ferrous oxide

	2	A	B	C	D
FeO	43·07	45·82	33·78	36·67	33·14
MgO	1·98	2·48	0·81	4·37	1·08
MnO	0·33	0·42	0·02	0·43	0·03
CaO	0·42	0·73	nil	0·16	—
Fe_2O_3	32·27	27·93	60·33	32·39	62·09
Al_2O_3	0·78	2·35	2·39	6·16	—
V_2O_3	1·74	0·92	0·54	0·86	0·68
Cr_2O_3	0·13	0·94	0·09	—	0·20
TiO_2	19·28	18·41	1·45	15·30	2·50
SiO_2	0·24	—	0·62	1·81	—
P_2O_5	0·03	—	—	0·03	—
S	—	—	—	0·02	—
H_2O	0·06	—	—	1·49	
TOTAL	100·33	100·00	100·03	99·69	99·72

2. Magnetite from rock 2308, Skaergaard (see Table 2).
A. Magnetite from dolerite, Södra Ulvön, Sweden (Mogensen, 1946). Composition of magnetite calculated from analyses of a high grade concentrate containing 1·61% SiO_2 (2·5% other minerals).
B. Magnetite from ilmenite norite, Storgangen, Norway. Anal. E. Klüver. (Foslie, 1928.)
C. Magnetite of magnetite-olivinite dyke, Taberg, Sweden. Anal. A. Aaremäe. (Hjelmqvist, 1950.)
D. Magnetite from amphibolite, Otanmäki, Finland. Anal. O. Vaasjoki. (Vaasjoki, 1947.)

and in three cases out of four an excess of FeO remains even if all the TiO_2 present is calculated into Fe_2TiO_4. The Taberg ore (analysis C) could be interpreted, as the Skaergaard 2308 (analysis 2) as containing ilmenite and ulvöspinel without further excess of FeO. The appreciable excess of uncombined FeO in the two titanium-poor magnetites (analyses B and D), and in the material from Ulvön (analysis A), is taken by the respective authors to indicate that free ferrous oxide remains in the magnetite lattice, and this seems the most likely explanation. A clear physical picture of the continuous oxidation series of cubic structures from FeO through Fe_3O_4 to γ-Fe_2O_3 has been given by A. F. Wells (1945, p. 334).

As far as the Skaergaard magnetites are concerned, the excess FeO present in most of them certainly seems to be combined in the Fe_2TiO_4 molecule, which is exsolved as ulvöspinel beyond a certain limiting concentration. No lines of the ferrous oxide pattern can be discerned in the X-ray photographs, while solid solution between Fe_3O_4 and Fe_2TiO_4, having the same structure type, seems more likely to occur than does the incorporation of free FeO, unless the latter oxide is present in such quantity as to remain in excess after all the available titanium has been combined in Fe_2TiO_4.

(c) *Ilmenites*

Chemical analyses of five ilmenites separated from the Skaergaard rocks, together with molecular proportions of the oxides, are given in Table 4.

Ilmenite has a rhombohedral lattice of the corundum type, and analyses of natural ilmenites and work on synthetic materials has shown that a certain proportion of sesquioxides having the same type of crystalline structure—notably Fe_2O_3—may remain in solid solution at ordinary temperatures. The value usually quoted for the maximum Fe_2O_3 thus held in solid solution is 6% (see, for example, Dana's "System of Mineralogy," 7th ed., 1944, p. 536). The X-ray powder photographs of the analyzed ilmenite concentrates show no lines other than those of the ilmenite pattern, but a few minute exsolution lamallae are to be seen with the ore-microscope in the ilmenite of some of the rocks, (see p. 13 above; also Part II).

In the case of the ilmenites, unlike the magnetites which are mixtures, the molecular proportions of divalent and tetravalent oxides in the analyses may be balanced as a check on the purity of the samples and the accuracy of the analyses. This has been done in Table 4, and the results seem satisfactory. The low total in ilmenite analysis 4142 may be due, in view of its satisfactory balance, to a low value for Fe_2O_3: this analysis was made on a total sample of about 80 mg.

5. Composition of the Analyzed Minerals and the FeO—Fe_2O_3—TiO_2 Thermal System

There is some published experimental work on solid solution relationships and thermal behaviour in parts of the FeO—Fe_2O_3—TiO_2 system. Grieve and White (1939) have given an account of the system FeO—TiO_2; but Greig *et al.* (1935) found that the system FeO—Fe_2O_3 presented unusual experimental difficulties, and they were unable to fix the eutectic compositions and temperatures between FeO and Fe_3O_4 or between Fe_3O_4 and Fe_2O_3. The relationships between

Table 4. Chemical analyses of ilmenites from the Skaergaard intrusion (Analyst: E. A. VINCENT) *(In ascending order in the layered series)*

Horizon:	Hypersthene-olivine-gabbro		Middle gabbro		Hortonolite-ferrogabbro		Ferro-hortonolite-ferrogabbro		Fayalite-ferrogabbro		$FeTiO_3$
Analysis No.:	9		10		11		12		13		
Rock No.:	2308 Melano-cratic band		3661		2569 Melano-cratic band		4147		4142		
Weight %											
FeO	39·64		40·39		42·72		43·30		42·18		47·35
MgO	3·27		2·27		1·48		0·62		0·46		
MnO	0·47		0·41		0·62		0·65		1·44		
CaO	0·37		0·34		0·48		0·46		0·71		
TiO_2	51·19		49·89		51·97		50·31		50·02		52·65
SiO_2	0·09		0·14		0·23		0·57		0·51		
Fe_2O_3	4·25		6·26		2·58		3·92		4·19		
Al_2O_3	0·17		0·02		nil		trace		n.d.		
V_2O_3	0·32		0·18		nil		nil		n.d.		
Cr_2O_3	nil		nil		nil		nil		n.d.		
H_2O	0·03		0·06		0·04		0·07		0·13		
TOTAL	99·80		99·96		100·12		99·90		99·64		100·00
Parts per million											
Zn	120		140		120		220		n.d.		
Cu	70		130		400		150		n.d.		
Molecular proportions ($\times$ 1000)											
FeO	552		562		595		603		587		
MgO	81	646	56	630	37	650	15	635	11	631	
MnO	6		6		9		9		20		
CaO	7		6		9		8		13		
TiO_2	641	643	625	627	651	655	630	639	626	634	
SiO_2	2		2		4		9		8		
Fe_2O_3	27		39		16		25		26		
Al_2O_3	2	31	—	40	—	16	—	25	—	26	
V_2O_3	2		1		—		—		—		

Fe_2O_3 and TiO_2 have more recently been discussed by ERNST (1943), who also gives a tentative picture of the boundaries between the stability fields of the various compounds in the FeO –Fe_2O_3—TiO_2 system at their melting points.

The chemical analyses of the Skaergaard magnetites and ilmenites have been plotted in terms of molecular percentages of the groups of oxides $FeO + MgO + MnO + CaO$; $Fe_2O_3 + Al_2O_3 + V_2O_3 + Cr_2O_3$; and $TiO_2 + SiO_2$, in a triangular diagram (Fig. 3) upon which the available thermal data for the relevant

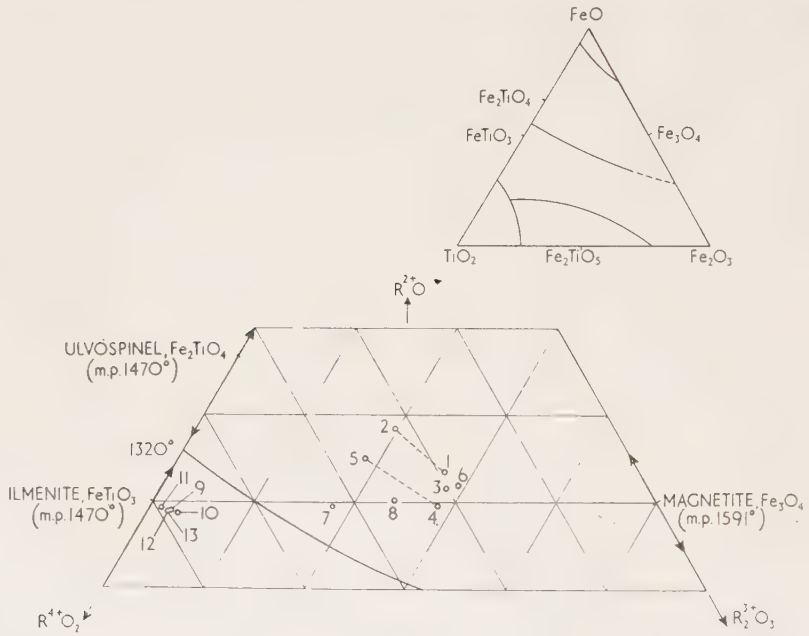


Fig. 3. Molecular percentages of groups of oxides in the Skaergaard magnetites and ilmenites. (Numbers represent analyses in Tables 2 and 4.) *Inset:* Stability fields of compounds in the FeO—Fe_2O_3 –TiO_2 dry thermal system at their melting points (after ERNST, 1943).

part of the FeO—Fe_2O_3—TiO_2 system in dry melt (assembled from the papers cited above) have been superimposed.

The close grouping and position of the ilmenite analyses emphasizes their closeness to pure $FeTiO_3$ in composition. (The positions of the plotted points are very little changed if only the molecular percentages of FeO, Fe_2O_3, and TiO_2 are used.)

Between the ilmenites and the magnetites there runs a valley in the dry thermal system, joining the $FeTiO_3$—Fe_2TiO_4 eutectic at 1320°C (GRIEVE and WHITE, 1939) and the yet undetermined Fe_3O_4—Fe_2O_3 eutectic. The exact position of this valley and its direction of slope cannot thus be fixed at present, but clearly all the Skaergaard magnetite analyses when plotted fall on a thermal surface sloping downwards towards the valley from a crest joining the pure compounds Fe_3O_4 and Fe_2TiO_4.

Although the slope cannot be contoured, and in any case would have rather a different configuration under magmatic conditions from those in dry melt, we

should anticipate that the magnetites from the earlier, higher temperature rocks of the layered series would lie nearer the crest, and the later ones nearer the valley, and this is found in general to be the case. The pairs of analyses 1 (2307) and 2 (2308), and 4 (2574) and 5 (2569), from average and dark bands at the same horizons, very probably lie on the same contour lines; but the two from the fayalite-ferrogabbros, 7 (1974) and 8 (4142) are not from quite the same horizons, and probably crystallized and exsolved at rather different temperatures, although both lie low down on the thermal slope. No satisfactory explanation can at present be offered for the anomalous position of the magnetite from the ferrohortonolite-ferrogabbro, analysis 6 (4147), which lies higher on the slope than would be expected.

6. Variations in Composition of the Iron-Titanium Oxides in the Light of the Skaergaard Differentiation Processes

Of the eight rocks from which magnetite, or both ilmenite and magnetite have been separated, all but the two melanocratic bands 2308 and 2569 may be regarded as fairly average representatives of their horizons within the layered series (see Wager and Deer, 1939, pp. 85–86; 117 ff.). The two melanocratic bands were originally selected for this work because of their richness in opaque oxides, favouring the separation and purification of these minerals in reasonable quantities. When the magnetites were analyzed, however, they proved abnormally rich in FeO compared with those in other rocks of the series. Professor L. R. Wager suggested that this high content of FeO might be connected in some way with the absolute quantity of opaque oxides in the dark bands, and kindly provided specimens (2307 and 2574) of more average rocks from the same horizons so that the magnetites in these could also be separated and analyzed.

The analyses of the magnetites and ilmenites are plotted on variation diagrams in Figs. 4 and 5. The variable taken as the abscissa is the percentage of the magma solidified at each particular stage of the genetic sequence, as estimated by Wager and Deer. It will be seen that if only the average rocks are considered, the minerals do not vary greatly in content of major oxides, whereas the variations among the minor constituents are much more striking, and reflect more closely the trends of differentiation of the Skaergaard magma.

Minor constituents of the magnetites and ilmenites

Spectrographic determinations of certain minor constituents of magnetites and ilmenites previously separated from this suite of rocks have been published, with a discussion of their variation and significance, by Wager and Mitchell (1951). New colorimetric determinations of vanadium, chromium, and copper have been made in the present investigation, and although the values obtained differ somewhat from the earlier spectrographic ones, they serve to confirm the broad conclusions drawn by Wager and Mitchell, and do not call for detailed discussion.

The figures obtained for vanadium in the magnetites by the colorimetric method are a good deal higher, however, than those obtained spectrographically (Wager and Mitchell, 1951, pp. 185–186). The writer has made duplicate or

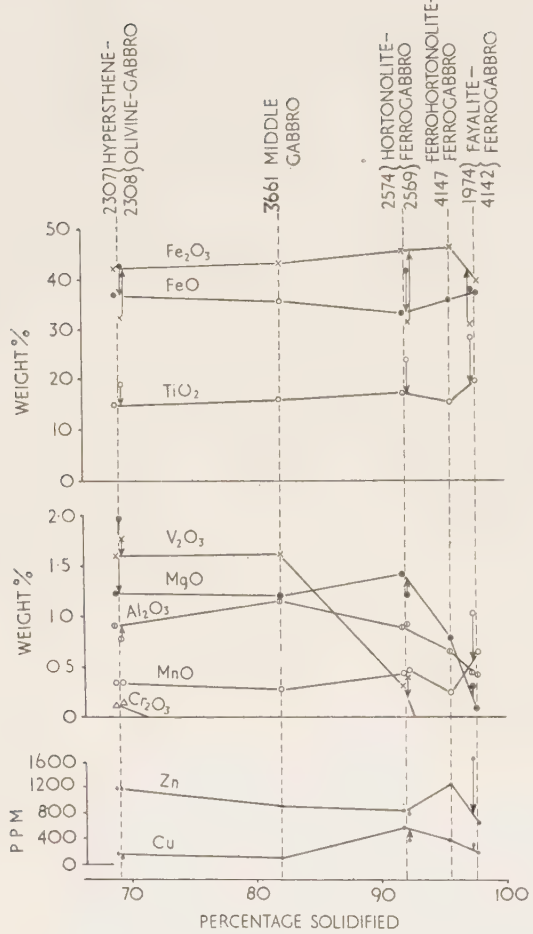


Fig. 4. Compositions of the analyzed Skaergaard magnetites.

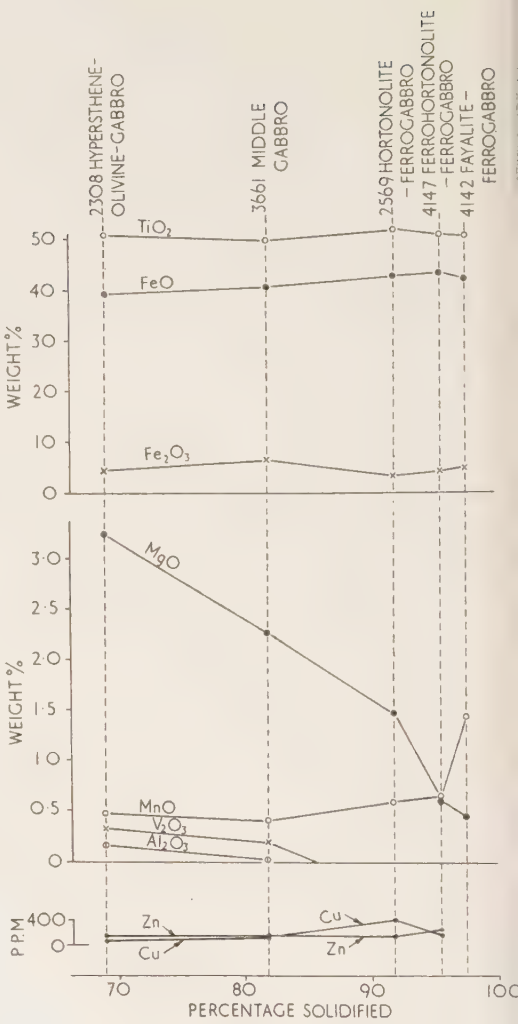


Fig. 5. Compositions of the analyzed Skaergaard ilmenites.

triplicate determinations with great care, and feels that the present values are reasonably correct for these samples.

Brief mention may be made of certain other elements present in these minerals, and which were not previously determined spectrographically.

Phosphorus was sought in the magnetites; it is present, but shows no significant variation.

Zinc was reported in the magnetites analyzed by Wager and Mitchell (1951, p. 158) but the spectrographic method was not sufficiently sensitive to yield reliable quantitative estimates. The present colorimetric determinations were made by the very sensitive dithizone method, and it was found possible to obtain good duplicate results. The amounts of zinc present in the magnetites are appreciable

(of the order of 0·1–0·2% Zn) but do not reach the order of 1% suggested by Wager and Mitchell (1951, Table B, footnote 2). The present determinations show that this element, as might be expected, had a strong preference for entering magnetite rather than ilmenite (see Tables 2 and 4; Figs. 4 and 5).

Lead was sought in all the magnetites, but is present, if at all, in quantities below the sensitivity of the determinations (about 20 p.p.m.).

Silicon is present in all the magnetite and ilmenite samples analyzed. In part, the SiO_2 content of the samples reflects the degree of contamination by silicates. On the other hand, certain of the ilmenite samples from which all visible composite grains containing transparent material were removed by hand-picking still contain as much as 0·5% SiO_2, which is considered more than could be accounted for by minute inclusions and veinlets of silicates in the opaque mineral grains. It seems possible, then, that a certain amount of silicon may enter the crystalline structures of these magnetites and ilmenites, perhaps sometimes replacing titanium; Rankin and Merwin (1918, p. 307) also recorded the presence of up to 2% SiO_2 in spinels synthesized in the course of their investigation of the system MgO—Al_2O_3—SiO_2. The values for silica have not been plotted in Figs. 4 and 5, because of this uncertainty.

Similar considerations may apply to calcium. Much of this element is doubtless present in the contaminating silicates, but there is no obvious direct correlation between the figures obtained for CaO and SiO_2, and there seems no reason why a limited amount of calcium should not enter the magnetite and ilmenite crystal structures. A similar conclusion was reached by Mogensen (1946, p. 587) with regard to the Södra Ulvön magnetite, which contains about 0·7% CaO.

In order to illustrate the rate of change of concentration of some of the geochemically related elements in these minerals, Figs. 6–9 have been prepared. The use of a logarithmic ordinate enables a real comparison to be made of the profiles of the variation curves, which are based upon Wager and Mitchell's earlier data for Ga, Co, and Ni, as well as upon the new analyses made for this paper. Oxides which are present in low concentrations have been multiplied by arbitrary factors for the sake of easy comparison. As the ordinate is logarithmic such multiplication merely displaces the curve, and in no way distorts it. A pair of parallel curves on a logarithmic scale shows that the ratio of the two oxides remains the same throughout the differentiated suite: this cannot be demonstrated using a linear scale.

Among the sesquioxides of the magnetites of the average rocks (Fig. 6), Al_2O_3 decreases through the series much less sharply than V_2O_3. Ga_2O_3 follows Al_2O_3 in the earlier stages, but deviates markedly above the hortonolite-ferrogabbro stage.

In the ilmenites, on the other hand (Fig. 7), Al_2O_3 decreases much more rapidly than V_2O_3; Ga_2O_3 does not appear to follow Al_2O_3. The variation in Fe_2O_3 in the ilmenite samples analyzed is not particularly logical. This may be because ilmenite was not separated from the average hypersthene-olivine-gabbro and hortonolite-ferrogabbro, but only from the ore-rich bands at these horizons, so that, by analogy with the corresponding magnetites it is possible that the ilmenites in 2307 and 2574 would prove to have slightly more Fe_2O_3 than those of 2308 and 2569 which have been analyzed.

In the magnetites of the average rocks MnO, ZnO, and CuO show rather

irregular variation (Fig. 8): in both magnetites and ilmenites manganese increases sharply in the later stages of the sequence.

MgO decreases steadily throughout the ilmenite series, while in the associated magnetites the decrease is rapid only in the later stages (Figs. 8 and 9). It is of interest that none of the magnetites carry much magnesium. Spinels rich in the

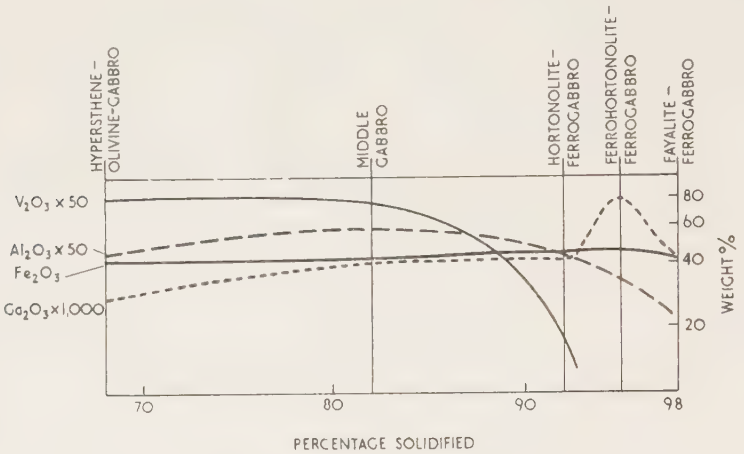


Fig. 6. Variation in sesquioxides of Skaergaard magnetites.

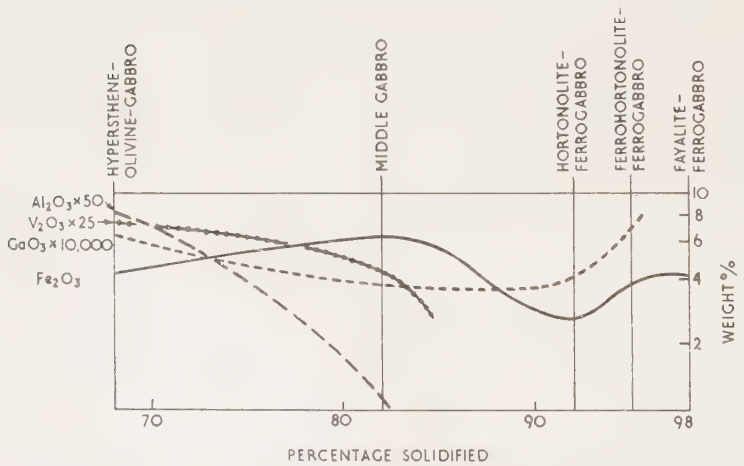


Fig. 7. Variation in sesquioxides of Skaergaard ilmenites.

magnesioferrite molecule are sometimes encountered as early-separating minerals from basic magmas (Fleischer, 1953, p. 156). The Skaergaard magma, however, was about 70% crystallized by the time sufficient ferric iron had accumulated for a ferrite spinel to appear as a primary phase in the hypersthene-olivine-gabbros, and by this stage a great part of the available magnesium had already been removed in the earlier olivines and pyroxenes. Ferrous iron greatly preponderates over magnesium in the rocks of the layered series, and the spinels crystallizing are likewise poor in magnesium.

There is a striking correspondence between the behaviour of MgO and CoO (Fig. 8), the ratio of one to the other remaining constant throughout the magnetite series. A rather similar, but less well marked correspondence is apparent in the ilmenites (Fig. 9). This close similarity in geochemical behaviour of Mg and Co has already been remarked in silicate rocks (Sandell and Goldich, 1943), and it is of some interest that it persists in these iron-titanium oxides. Ni does not seem to follow Co in the opaque minerals; it behaves similarly in both magnetite and ilmenite series.

Major constituents of the magnetites

The variation in the three principal oxides FeO, Fe_2O_3, and TiO_2 is remarkable, when all the analyzed magnetites are considered. Firstly, there is a great difference in the degree of oxidation of the iron between magnetites from average and melanocratic bands of the same horizon, and secondly the higher titanium content of the ferrous-rich magnetites. The abnormally low Fe_2O_3 and high TiO_2 content of the magnetite from the fayalite-ferrogabbro 1974 reflects the absence of discrete ilmenite crystals in this rock; both 1974 and 4142 are reasonably average rocks in overall mineralogical composition. It is hoped later to study the opaque minerals in these higher rocks of the layered series in more detail.

With a given amount of iron and titanium available in the melt from which the minerals crystallize, it is apparent in a general way that the degree of oxidation of the iron[1] will determine whether solid solutions between Fe_3O_4 and $FeTiO_3$, or between Fe_3O_4 and Fe_2TiO_4, or mixtures of both types, will be formed at high temperatures.

Foslie (1928) made the suggestion that many cases of exsolution of ilmenite from magnetite might well be the result of subsequent oxidation of an Fe_3O_4—Fe_2TiO_4 solid solution. At that time, ulvöspinel was unknown in nature, but V. M. Goldschmidt (1926) had already suggested that the synthetic Fe_2TiO_4 had a spinel structure like Mg_2TiO_4, which was well known. Foslie wrote down the possible behaviour of Fe_2TiO_4 under oxidizing conditions in this form:

$$Fe_2TiO_4 + Fe_2O_3 \rightarrow Fe_3O_4 + FeTiO_3,$$

and remarked that apparently Fe_2TiO_4 could only form and remain stable under conditions where there was no excess of Fe_2O_3 present. Some confirmation for this kind of oxidation reaction is provided by the magnetites of the Skaergaard hypersthene-olivine-gabbros 2307 and 2308, and the middle gabbro 3661, in which lamellae of ulvöspinel are seen with the microscope to have partly changed over to ilmenite (see p. 5, above).

In his discussion of the iron-bearing basalt of Bühl, Ramdohr (1953a, pp. 15–16) considers that ulvöspinel may at times be formed by reduction of ilmenite; that in the presence of oxygen it oxidizes to ilmenite plus magnetite; and that in

[1] It is assumed that the titanium is tetravalent in these minerals. It is impossible in analysis to distinguish between $Ti^{4+} + Fe^{2+}$ and $Ti^{3+} + Fe^{3+}$ in the solid; $Ti^{4+} + Fe^{2+}$ is always obtained in solution, and the distinction is immaterial for many purposes. Chevallier and Girard (1950) suggest that ilmenite in the crystalline state is a statistical equilibrium between the two forms $Fe^{3+}Ti^{3+}O_3$ and $Fe^{2+}Ti^{4+}O_3$, and that its magnetic properties favour the concept of such a mesomerism.

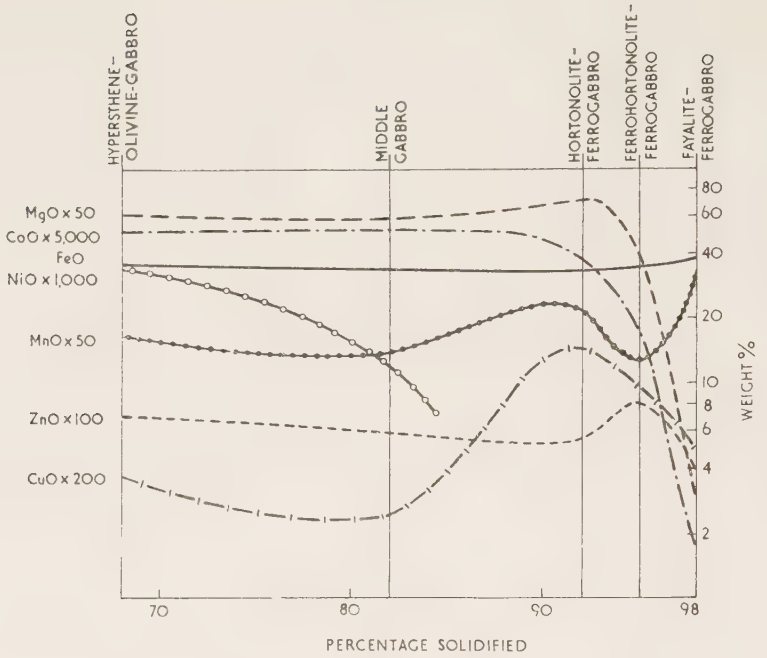


Fig. 8. Variation in protoxides of Skaergaard magnetites.

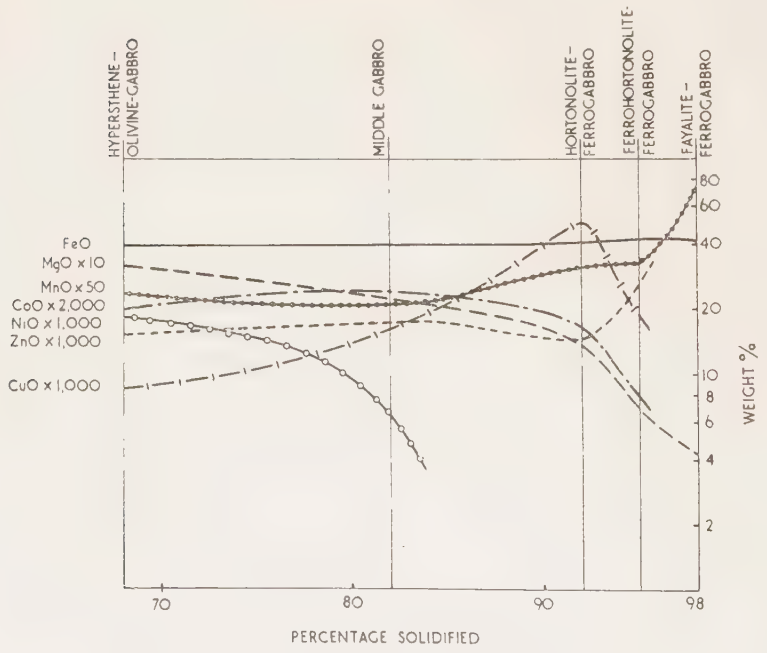


Fig. 9. Variation in protoxides of Skaergaard ilmenites.

other circumstances, in the absence of oxygen, it may decompose into an aggregate of magnetite, ilmenite, and metallic iron.

Oxidation-reduction relationships between Fe_3O_4, Fe_2TiO_4, and $FeTiO_3$ seem reasonable in the light of their crystalline structures. The ilmenite lattice is in effect a hexagonal close-packing of oxygen atoms in which two-thirds of the holes are occupied by Fe and Ti atoms in octahedral co-ordination. In the spinel structures of Fe_3O_4 and Fe_2TiO_4 (Barth and Posnjak, 1932) the oxygens are arranged in cubic close-packing, with metal atoms in tetrahedral and octahedral co-ordination; the oxygen layers parallel to (111) in the spinel structures and parallel to (0001) in the ilmenite structure are practically equivalent. The textures of the minerals in the Skaergaard rocks, also, may perhaps be taken to indicate that oxidation of Fe_2TiO_4, or an Fe_3O_4—Fe_2TiO_4 solid solution, to a product containing ilmenite need not necessarily take place under conditions where the crystal lattice structure is strictly preserved during the process. The oxidation and early stages of the exsolution may well have proceeded concurrently.

The contrast in the state of oxidation of the iron in the magnetites is strikingly shown by the two examples 2307 and 2308 from the hypersthene-olivine-gabbro horizon. If the analyses are compared (Table 2, analyses 1 and 2), it will be noted that the differences are in the contents of FeO, Fe_2O_3, TiO_2, and to a less extent MgO. Other oxides—notably MnO, Al_2O_3, V_2O_3, and Cr_2O_3—are very similar in the two analyses, and the values for the minor constituents seem characteristic of the magnetite of the hypersthene-olivine-gabbro as a whole at this horizon. A similar comparison may be made of the two magnetites from the hortonolite-ferrogabbro horizon, 2574 and 2569. Only the balance between iron oxides and titanium is different, the ratio of ferric to ferrous iron being considerably higher in the magnetite of the average rock.

Analyses of the two rocks themselves, however, show that the ratio of ferric to ferrous iron in the average rock 2307 is slightly less than in the melanocratic band. Presumably this is because most of the iron in the average rock is combined in the ferrous state in silicates, while in the melanocratic material a relatively higher proportion is bound with ferric oxide in magnetite, and the ratio of magnetite to silicates is here much greater. Once ferrous iron has entered the crystalline silicate structure of olivine or pyroxene, it is bound in that state of oxidation, and a change in the oxidizing power of its surrounding medium is unlikely to affect it to any appreciable extent, whereas it is suggested that the iron of the opaque oxide minerals is able to maintain an oxidation-reduction equilibrium with its surroundings at high temperatures.

It is not easy to understand the conditions in the crystallizing Skaergaard magma which could lead to the titaniferous magnetites being oxidized in an average band and strongly reduced in an adjacent melanocratic one. The mechanisms responsible for the rhythmic layering are not yet known in all their detail; Wager and Deer (1939, pp. 272–273) consider the phenomenon to be mainly due to varying velocity and intermittent nature of the convection currents in the magma.

It seems likely that the interstitial magmatic solutions, by virtue of the partial dissociation of water at high temperatures, determined the oxidizing or reducing atmosphere with which the oxide minerals maintained equilibrium (Kennedy, 1948).

and these may have been different, in quantity, quality, or both, in the average and adjacent melanocratic bands at the time the minerals finished crystallizing. In both types of band, most of the iron-titanium oxide minerals were formed as part of the primary precipitate, and under conditions of slow consolidation, the compositions of these minerals might continually change by oxidation-reduction reactions to maintain equilibrium with the partial pressure of oxygen in the surrounding inter-precipitate liquid as this gradually solidified.

If we make the reasonable assumption that the opaque minerals now found in the average and ore-rich bands both had the same composition when they first crystallized from the magma the question arises whether the magnetite in the average rock has been formed by oxidation of material resembling that in the melanocratic, or whether the magnetite of the melanocratic band has been formed from material such as that of the average band by a process of reduction. The passing over of the cloth-like intergrowth of ulvöspinel and magnetite into lamellae of ilmenite seen in the magnetites of the hypersthene-olivine-gabbros and middle gabbro, and the persistence of lamellar exsolution bodies of ilmenite in the higher magnetites, suggests that some at least of this ilmenite has been formed later than, and at the expense of, ulvöspinel, by an oxidation process. Further, if there were any general tendency for the inter-precipitate liquids to exert a reducing influence on the iron oxides, it would be expected that the magnetites of the average rocks would be more strongly reduced than those of the ore-rich bands, since the ratio of interstitial liquid to magnetite would be greater in the average rocks.

It seems likely that oxidation by the inter-precipitate magma was the dominant process; the whole question is one of attaining oxidation-reduction equilibrium between ore minerals and liquid.

Differences in the degree of oxidation of the iron in the magnetites due to the magmatic atmosphere with which they eventually attained equilibrium might be explained in various ways. Firstly, the proportion of inter-precipitate liquid to primary precipitate crystals may have been greater in the average rocks than in the melanocratic bands. Secondly, the two types of band may have contained comparable quantities of inter-precipitate liquid, but the amount of iron-titanium oxide minerals in the melanocratic was so great that the available partial pressure of oxygen was insufficient to maintain them in a high state of oxidation. Thirdly, the $FeO—Fe_2O_3—O_2$ equilibrium may have been attained at different temperatures or pressures in the two types of band, so that even if the proportions of interstitial liquid were comparable the partial pressure of oxygen may have differed in the two cases.

Some slight support for the first of these possibilities is afforded by a comparison of the phosphorus contents of the rocks 2307 and 2308. The average hypersthene-olivine-gabbro 2307 contains 0·13% P_2O_5 while the melanocratic band 2308 contains less than 0·01%. (New analyses of these rocks have been made by the writer.) Wager and Deer (1939, pp. 128; 227) consider that apatite is an inter-precipitate mineral at this stage in the intrusion, and it may be that some of the difference in phosphorus contents of the two rocks is due to different amounts of inter-precipitate liquid having been involved in their final crystallization.

It is not yet clear why the magnetites of the melanocratic bands 2308 and 2569 should be significantly richer in titanium than those of the corresponding average rocks, as well as in ferrous iron. The titanium content of the magnetites is probably to some extent related to the amount of discrete ilmenite coexisting in the rock, but the correlation does not seem to be particularly simple.

It is worthy of note that other magmatic rocks in which Fe_2TiO_4 enters the magnetite in appreciable quantity, or in which the magnetite carries an excess of ferrous oxide, are also very rich in opaque oxide minerals, just as the melanocratic bands in the Skaergaard intrusion. The rock mined at Södra Ulvön (Table 3; Mogensen, 1946) is a dolerite with 53% by volume of ore minerals; the ilmenite-norite investigated by Foslie (1928) has 36% ilmenite and 5% magnetite; while the magnetite-olivinite of Taberg, investigated by Hjelmqvist (1950) appears to carry about 40% of opaque oxides.

The association of a high concentration of iron-titantium oxides and a low state of oxidation of the iron contained in them, so well displayed by the Skaergaard rocks, may therefore prove to be widespread, and due in each case to similar causes.

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Iron-titanium oxide minerals in layered gabbros of the Skaergaard intrusion, East Greenland

Part II. Magnetic properties

Raymond Chevallier and Suzanne Mathieu

Laboratoire de Physique de la Faculté des Sciences, Université de Nancy,

and E. A. Vincent

Department of Geology and Mineralogy, University Museum, Oxford.

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ABSTRACT

Measurements of the magnetic constants of chemically analyzed titaniferous magnetites from the Skaergaard intrusion indicate that $FeTiO_3$ is completely exsolved as ilmenite lamellae. Up to about 6% Fe_2TiO_4, however, may remain in solid solution, the amount appearing to be more closely related to the temperature of consolidation of the rock than to the total Fe_2TiO_4 content of the mineral.

The magnetic measurements provide a completely independent estimate of the Fe_3O_4 contents of the samples, which show good agreement with values calculated from chemical analyses.

The coexisting ilmenites show little variation in magnetic properties; in particular there is no close relationship between magnetic properties and content of Fe_2O_3.

1. Introduction

This paper describes the magnetic properties of a series of opaque minerals (titaniferous magnetites and ilmenites) which were separated by one of us (E. A. V.) from a suite of gabbros and ferrogabbros of the Skaergaard intrusion, East Greenland. An account of their chemistry and ore-microscopy, with a discussion of their genesis, has been given by Vincent and Phillips (1954) as Part I of this work; this further study of the magnetic properties of the minerals has been carried out by the first-named authors, the last-named having helped in correlating the results with those of the microscopic and chemical work and prepared the English text.

Chemical analyses of the magnetites, with formal recalculations, were given in Part I, Table 2. Table 5, below, summarizes the results of chemical, X-ray, and microscopic examination of these minerals.

The ilmenite samples are less complex in composition than the magnetites (Part I, Table 4) and their analyses are not reproduced here.

2. Magnetic Properties of the Titaniferous Magnetites

Two different types of magnetic measurement have been made upon each sample.

1. The magnetization curve at 20°C has been determined, up to a field strength of 6500 gauss, by a method described by Chevallier and Mathieu (1943). At this field strength saturation has to all intents and purposes been reached. The intensity of magnetization, σ_l, in electromagnetic units referred to 1 g of sample for this field strength of 6500 gauss has been recorded, and very closely approximates to the saturation magnetization.

Table 5. Composition of the analysed Skaergaard magnetites

Analysis No. (Pt. I, Table 2)	*Rock No. E.G.*	*Principal constituents, calculated from analysis*			*Phases revealed in X-ray photographs*	*Phases revealed by ore-microscope*
		Fe_3O_4 %	Fe_2TiO_4 %	$FeTiO_3$ %		
1	2307	56·0	16·3	18·1	magnetite, ulvöspinel, ilmenite	magnetite, ulvöspinel, ilmenite
2	2308	35·3	43·4	7·1	magnetite, ulvöspinel, ilmenite	magnetite, ulvöspinel, ilmenite
3	3661	57·3	7·9	25·5	magnetite, ?ulvöspinel, ilmenite	magnetite, ulvöspinel, ilmenite
4	2574	59·7	0·0	30·8	magnetite, ilmenite	magnetite, ilmenite
5	2569	39·9	24·4	28·5	magnetite, ulvöspinel, ilmenite	magnetite, ulvöspinel, ilmenite
6	4147	61·5	9·5	22·2	magnetite, ilmenite	magnetite, ilmenite
7	1974	41·8	0·0	52·5	magnetite, ilmenite	magnetite, ilmenite
8	4142	55·3	2·7	35·5	magnetite, ilmenite	magnetite, ilmenite

2. A photographic record has been taken of the variation in magnetic moment of each sample as a function of temperature, in a constant magnetic field of about a hundred gauss. The apparatus and method used have been described by Chevallier and Pierre (1932), and some of the photographically recorded thermomagnetic curves are reproduced and discussed in a later section of the paper. From these curves, the temperature at which the ferromagnetism of the sample disappears (the Curie point, θ°C) can be read off.

The results of these measurements are embodied in columns 3 and 4 of Table 6.

The ferromagnetic spinel of the magnetite samples

The magnetites all show a single, unique, Curie point, giving rise to a very abrupt change of slope in the thermomagnetic curves (as in Fig. 10), proving the presence of but a single homogeneous ferromagnetic phase. If more than one such phase were present, the curve would have the appearance shown in Fig. 11; while if

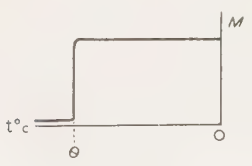

Fig. 10

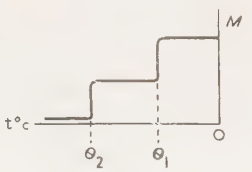

Fig. 11

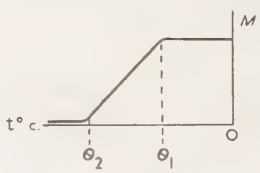

Fig. 12

Figs. 10–12. Possible forms of thermomagnetic curves for magnetites.

there were solid solutions of continuously varying composition, the curve would show a gradual slope, as in Fig. 12. Neither of these latter cases is found, and in all the present samples the Curie point is close to that of pure magnetite, Fe_3O_4.

Previous studies made by the authors on *homogeneous* crystals of titaniferous magnetite have shown that in these the Curie point and the saturation magnetization at 20°C, σ_∞, are governed by the concentration, f, of Fe_3O_4 in the material, whatever the nature of the other oxides in solid solution. Knowledge of the Curie point, therefore, enables us to evaluate σ_∞ and f for the spinel responsible for the ferromagnetism of our Skaergaard samples; these values have been calculated and are given in columns 5 and 6 of Table 6. (For pure Fe_3O_4, $\theta = 583$°C, $\sigma_\infty = 93$ e.m.u. per g sample.)

Table 6. Magnetic properties of the analysed Skaergaard magnetites

1	2	3	4	5	6	7	8	9	10
		Magnetic constants		*Calculated from magnetic constants*					Fe_3O_4 *calculated from analysis*
Analysis No. (Pt. I, Table 2)	*Rock No. E.G.*	θ	σ_l	σ_∞	f	$\frac{100\sigma_l}{\sigma_\infty}$	$f\frac{\sigma_l}{\sigma_\infty}$	$100\frac{\sigma_l}{93}$	
		°C	*e.m.u.*	*e.m.u.*	%	%	%	%	%
—	Magnetite, Kirunavaara	583		93	100				
1	2307	560	46·5	85	94·2	54·7	**51·5**	50·0	**56·0**
2	2308	562	33·6	85·5	94·8	39·3	**37·2**	36·2	**35·3**
3	3661	568	50·5	87·7	96	57·6	**55·3**	54·3	**57·3**
4	2574	580	55·8	93	100	60·0	**60·0**	60·0	**59·7**
5	2569	567	36·9	87·5	96	42·2	**40·5**	39·7	**39·9**
6	4147	574	58·2	90·5	98	64·4	**63·1**	62·6	**61·5**
7	1974	583	35·0	93	100	37·6	**37·6**	37·6	**41·8**
8	4142	581	50·3	93	100	54·2	**54·2**	54·2	**55·3**

Column 3. Curie point, θ°C.
4. Saturation magnetization, σ_l, of sample, in electromagnetic units.
5. Saturation magnetization, σ_∞, of the ferromagnetic spinel contained in the titaniferous magnetite.
6. Percentage, f, of Fe_3O_4 in the ferromagnetic spinel element of the titaniferous magnetite.
7. Percentage of ferromagnetic spinel in the magnetite, $100\frac{\sigma_l}{\sigma_\infty}$.
8. Percentage Fe_3O_4 in the magnetite.
9. Percentage Fe_3O_4 in the magnetite, supposing the ferromagnetic spinel to be pure Fe_3O_4.
10. Percentage Fe_3O_4 in the magnetite, calculated from chemical analysis.

Further, the expression $100\frac{\sigma_l}{\sigma_\infty}$ will give the proportion of ferromagnetic spinel present in the titaniferous magnetite (column 7) and $f\frac{\sigma_l}{\sigma_\infty}$ the percentage of Fe_3O_4 in the mineral as a whole (column 8). These estimates of the Fe_3O_4 contents of the samples, derived exclusively from physical measurements of their magnetic properties, are in remarkably good agreement with the values calculated from the chemical analyses (column 10), especially when it is borne in mind that the recalculation of the analyses is of necessity somewhat arbitrary (see Part I, Table 2). The agreement can perhaps be taken as some mutual check of the accuracy of the magnetic measurements and of the validity of the formal recalculation used.

The values of σ_∞ and f, deduced from the Curie point measurements, are based upon a limited number (about 20) of as yet unpublished measurements made on homogeneous titaniferous magnetites: if we had assumed as a first approximation that the ferromagnetic spinel present in the Skaergaard samples was pure magnetite, then the percentage Fe_3O_4 in each sample would be given by $100\frac{\sigma_\infty}{93}$. These figures (column 9) are also in fairly good agreement with the chemical estimates.

Table 7.

Analysis No.:	1	2	3	4	5	6	7	8
	Hypersthene-olivine-gabbro		Middle gabbro	Hortonolite-ferrogabbro		Ferro-hortonolite-ferrogabbro	Fayalite-ferrogabbro	
Rock No.	2307	2308	3661	2574	2569	4147	1974	4142
Calculated Fe_2TiO_4, %	16·3	43·4	7·9	0·0	24·4	9·5	0·0	2·7
Ulvöspinel in X-ray photograph	+	+	?		+			
Ulvöspinel visible with microscope	+	+	+		+			
θ°C	560	562	568	580	567	574	583	581
Mean θ°C	561		568	573		574	582	
$100 - f$ (% Fe_2TiO_4 remaining in solid solution in magnetite)	5·8	5·2	4·0	0·0	4·0	2·0	0·0	0·0

Higher ——————————→ *Lower*

Temperatures of consolidation of rocks

Microscopic and X-ray examination of the Skaergaard magnetites has revealed in some cases the presence of ulvöspinel, Fe_2TiO_4, as an exsolved phase, and its quantity can also be estimated by recalculation of the chemical analyses (see Table 5, above). The magnetites also contain lamellae of ilmenite, and we can be almost certain that all the $FeTiO_3$ in the minerals is present in these exsolution bodies. In particular, the ferromagnetic spinel element cannot contain any $FeTiO_3$ in solid solution, since in the magnetites 2574 and 1974 (analyses 4 and 7) in which there is no calculated Fe_2TiO_4, but appreciable calculated $FeTiO_3$, the

Curie points are nearly identical with one another (580° amd 583°C) and with that of pure Fe_3O_4.

On the other hand, the Curie point deviates farther from 580°C in those magnetites containing appreciable amounts of the Fe_2TiO_4 molecule (Table 7), but this deviation seems to have no obvious direct connexion with the quantities of other elements such as V, Cr, Al, or Mg (Part I, Table 2) which may enter into the structure of the spinel blend of the magnetites.

These observations seem to indicate that all the $FeTiO_3$ contained in the magnetites exists in the free state as exsolved ilmenite, and that the ferromagnetic spinel host consists of magnetite sometimes carrying a little Fe_2TiO_4 in solid solution (Table 7), while the excess of Fe_2TiO_4 is all exsolved as the non-ferromagnetic ulvöspinel.

The case of the magnetite from the ferrohortonolite-ferrogabbro 4147 (analysis 6) is unusual. The analysis shows an excess of FeO corresponding to a content of 9·5% Fe_2TiO_4, and the magnetic properties show that not more than 2% of this remains in solid solution. The remaining 7·5% has not been detected as an exsolved phase, either with the microscope or by X-rays. It was suggested in Part I that, if present as such, the ulvöspinel is in too fine a state of subdivision to be visible.

There is another matter of interest in the Curie point measurements. The pairs of rocks joined by brackets in Table 7 are from the same horizons in the Skaergaard intrusion, and, except for the hortonolite-ferrogabbros 2574 and 2569, their magnetites have the same Curie points. If the mean values of θ for each horizon are considered (including 2574 and 2569) they are seen to increase from bottom to top of the layered series—i.e. with decreasing temperatures of consolidation of the rocks. It is with some hesitation that we point out this relationship, since the differences between our Curie points are quite small, and the temperatures themselves cannot be fixed with absolute precision.

However, a general decrease in the amount of Fe_2TiO_4 remaining in solid solution in the magnetites as the layered series is ascended is quite in accord with suggestions made in Part I concerning the phase relationships between Fe_3O_4 and Fe_2TiO_4, and the observed steady increase in Curie point may well be a real and significant phenomenon. If so, the amount of Fe_2TiO_4 remaining in solid solution in the magnetites, while always small, seems to be more closely related to the temperature of consolidation of the rock than to the total Fe_2TiO_4 content of the mineral: those magnetites which crystallized and exsolved at the highest temperatures retaining most Fe_2TiO_4 in solution.

The role of magnesium in the magnetites

Magnesium is present in the magnetites of the lower and middle rocks of the layered series in quantities between 1 and 2% MgO. In the arbitrary recalculations of the analyses (Part I, Table 2) magnesium has mainly been allotted to the magnesioferrite molecule, $MgFe_2O_4$, which in the magnetite of the ore-rich hypersthene-olivine-gabbro 2308 reaches a calculated concentration of about 8%. This ferrite cannot be present in the free state in the magnetite, since it is a ferromagnetic spinel the Curie point of which, 350°C, does not appear on any of the thermomagnetic curves. It may be that $MgFe_2O_4$ exists in solid solution,

possibly in the ulvöspinel (since the Curie points of the magnetite samples seem directly related to Fe_2TiO_4 content, rather than to that of $MgFe_2O_4$), and is there sufficiently diluted for its ferromagnetic properties not to appear. The same remark applies to other ferrites implied by the chemical analyses.

Otherwise, the MgO could on recalculation be assigned to a "titanate." In this case, Fe_2O_3 would become available, and if this oxide were allotted to extra Fe_3O_4, the increased amount of calculated magnetite would no longer correspond so well with that deduced from the magnetic measurements.

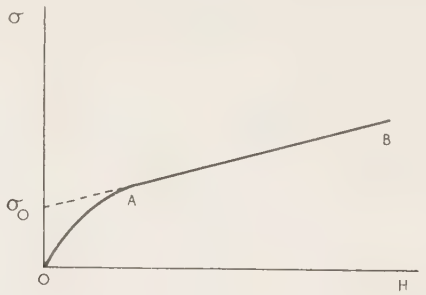

Fig. 13. Form of magnetization curve for the ilmenite samples.

Possibly the available magnesium is distributed more or less equally between the magnetite, ulvöspinel and ilmenite phases in these minerals. We cannot at present give a satisfactory explanation of the role of this element.

3. Magnetic Properties of the Ilmenites

All the ilmenite samples give a magnetization curve of the type shown in Fig. 13. For a magnetic field H of sufficient intensity the curve becomes linear (portion AB) and the magnetization law may be stated in the linear form

$$\sigma = \sigma_0 + \chi H$$

The ordinate σ_0 at the origin represents the spontaneous ferromagnetism of the sample, and, with the paramagnetic coefficient χ, is referred to 1 g of material. Table 8 shows the measured values of σ_0 and χ in electromagnetic

Table 8. Magnetic properties of the analysed Skaergaard ilmenites

Analysis No.	*Rock No.*	σ_0 *e.m.u.*	$10^6\chi$ *e.m.u.*	*Remarks*
—	—	0·0	96	Synthetic ilmenite
9	2308	0·45	111	Sample gave thermomagnetic curve
10	3661	$0{\cdot}01_5$	104·7	Sample gave no thermomagnetic curve
11	2569	0·06	98·6	Sample gave no thermomagnetic curve
12	4147	0·05	106·2	Sample gave no thermomagnetic curve
13	4142	$0{\cdot}01_5$	104·7	Sample gave no thermomagnetic curve

units for the various samples, and also for a pure synthetic ilmenite of composition $FeTiO_3$, without Fe^{3+} ions. This synthetic material has no spontaneous ferromagnetism.

The ferromagnetic susceptibility, σ_0, in the natural minerals could either be an intrinsic property of homogeneous ilmenite, or else due to the presence of a trace of magnetite as a separate phase. It was found possible to record a thermomagnetic curve for the ilmenite of rock 2308 (Part I, Table 4, analyses 9), which shows a very much stronger spontaneous ferromagnetism than the remaining samples (Fig. 15F). There is no sharp, precise, Curie point, but a continuous slope steepening suddenly between 520° and 560°C, thus terminating at the Curie point of the magnetite in the same rock (Table 6). It thus appears most likely that the source of this ferromagnetism is a trace of titaniferous magnetite of some kind.

In the account of the microscopic characters of these minerals it was mentioned (Part I, p. 3) that the ilmenite in this rock 2308 carried very narrow anisotropic lamellae whose optical characters suggested that they might be a solid solution between $FeTiO_3$ and Fe_3O_4. Lamellae of such composition would perfectly explain the thermomagnetic curve: the fine dispersion of the material provides a good reason for the regular slope of the curve and the rather vague Curie point. The sample does not yield a thermomagnetic curve of the type found for the coexisting magnetite, which would be expected if the ferromagnetism of the ilmenite sample were mainly due to imperfect separation of the two materials from the rock.

The ferromagnetism of the ilmenite 2308 is due to quite a small amount of magnetite, of the order of $\frac{\sigma_0}{\sigma_\infty} = \frac{0{\cdot}45}{93} = 0{\cdot}48\%$ Fe_3O_4. Subtraction of this amount of Fe_3O_4 from the chemical analysis of the ilmenite (Part I, Table 4, analysis 9) does not appreciably alter the balance of tetravalent and divalent oxides. The very slight ferromagnetism exhibited by the remaining ilmenite samples is doubtless mainly due to similar, but less numerous or smaller lamellae observed with the microscope. The values of σ_0 indicate that the amounts of magnetite they contain must be at least ten times less than in 2308.

The paramagnetism, on the other hand, is an intrinsic property of the ilmenite host crystals themselves. The coefficients χ in Table 8, while very close to that of the synthetic material are always a little greater, pointing to the presence of Fe^{3+} ions in the lattice. However, there seems no obvious connexion between the percentage of Fe_2O_3 in the ilmenite analyses (Part I, Table 4) and the value of χ. Possibly a part of the Fe_2O_3 is present as free haematite, but it has not been detected as a separate phase under the microscope.

4. The Thermomagnetic Curves

The photographically recorded thermomagnetic curves, some of which are reproduced in Fig. 15, were obtained in a constant magnetic field of the order of 100 gauss. The magnetic moment M of the sample is represented by the ordinate, the temperature, t°C, by the abscissa. At the Curie point, θ°C, the moment M falls to zero (Fig. 14). The breaks in the photographic records mark each hundred

degrees. and the beginnings of the breaks (in the sense 0–t in Fig. 14) are at exactly 100°, 200°, 300°, 400°, 500°, and 620°C. The Curie point may thus be determined with precision when it is sharp. In most of the photographs, one curve represents the sample being heated (t increasing), the other cooling.

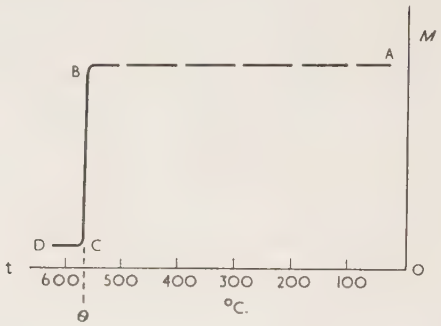

Fig. 14. Explanatory diagram of thermomagnetic curves for magnetite.

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DETAILED LEGENDS TO FIGS. 15 A–F (OPPOSITE)

Fig. 15A. *Pure magnetite from Kirunavaara, Sweden.* (*Reference standard*). Magnetic field maintained both during heating and cooling.

Note—

(1) The sudden disappearance of ferromagnetism. The magnetic couple balancing the torsion in the apparatus disappears so rapidly that the indicating light beam oscillates on returning to zero. In the CD part of the curve (see Fig. 14) this oscillation is being mechanically damped.

(2) The vertical portions BC of the curves are exactly superimposed on heating and cooling. This is rare, and indicates the absence of any thermal hysteresis. The Curie point is 582°C.

(3) The horizontal portions AB of the curves corresponding to heating and to cooling are not superimposed: there is slight thermoremanent magnetism apparent on cooling.

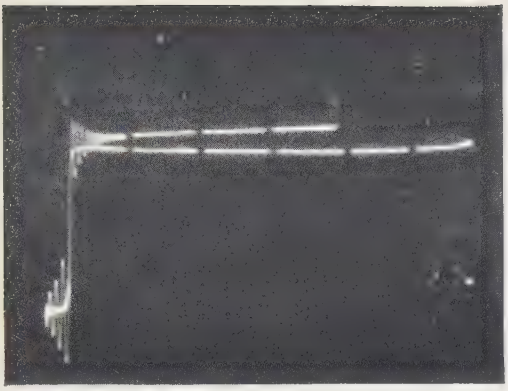
Fig. 15B. *Magnetite* 2307 (*analysis* 1). Magnetic field maintained both during heating and cooling. Here, the vertical parts of the curves are not exactly superimposed, and there is very slight thermal hysteresis. The oscillation to be observed in the heating curve indicates a sharp Curie point—mean value 560°C. The sample shows greater thermoremanence than the standard.

Fig. 15C. *Magnetite* 2308 (*analysis* 2). Magnetic field maintained both during heating and cooling. No thermal hysteresis. Very sharp Curie point at 562°C. The sample again shows appreciable thermoremanence.

Fig. 15D. *Magnetite* 4147 (*analysis* 6). Magnetic field maintained both during heating and cooling. This sample shows appreciable thermal hysteresis and thermoremanence. Curie point 574°C on the heating curve.

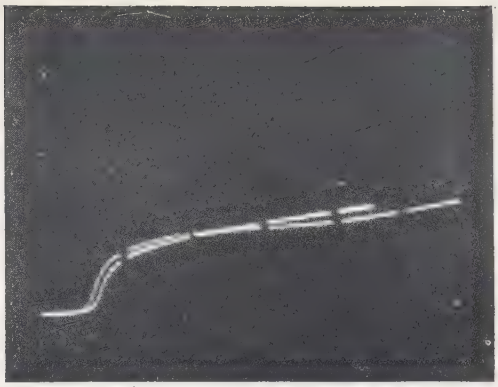
Fig. 15E. *Magnetite* 1974 (*analysis* 7). Magnetic field maintained only on *cooling*. The Curie point, 583°C, is that of pure Fe_3O_4. (The trace of the Curie point on the heating curve is due to the residual magnetic field of the pole-pieces of the electromagnet used in the apparatus.)

Fig. 15F. *Ilmenite* 2308 (*analysis* 9). Magnetic field maintained both on heating and cooling. The curve is quite different from that of the magnetite in the same rock (Fig. 15C). The magnetic moment decreases regularly up to 500°C. From 520°C the slope increases, and ends at about 560°C. There is no sharp Curie point.



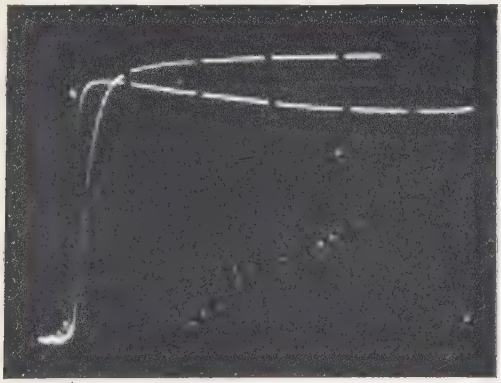
$\theta = 582°C$

A
Magnetite, Kirunavaara



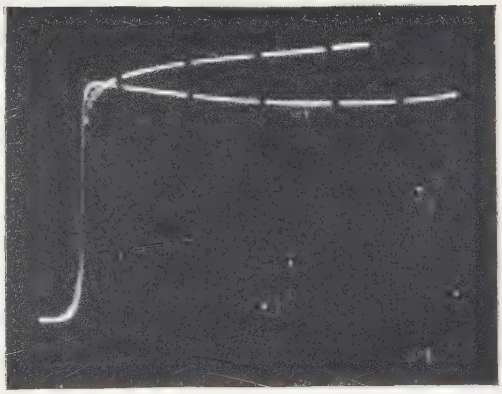
$540° < \theta < 560°C$

F
Ilmenite, 2308



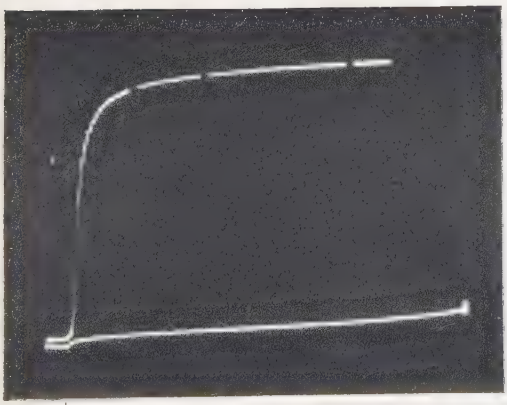
$\theta = 574°C$

D
Magnetite, 4147



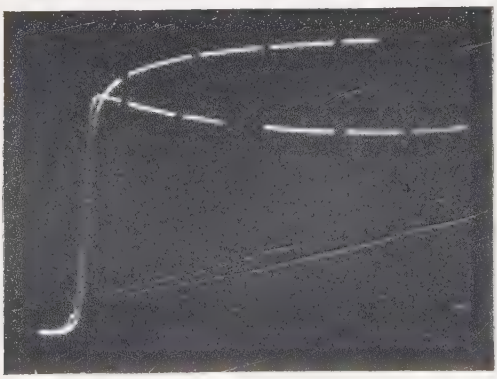
$\theta = 562°C$

C
Magnetite, 2308



$\theta = 583°C$

E
Magnetite, 1974



$\theta = 560°C$

B
Magnetite, 2307

Fig. 15. Thermomagnetic curves for Skaergaard ore minerals.

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Geochemistry of molybdenum

P. K. Kuroda* and E. B. Sandell

School of Chemistry, University of Minnesota, Minneapolis

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ABSTRACT

Chondrites have rather uniform molybdenum contents; the average of 14 specimens is 1·6 p.p.m. Mo, with the range 1·2–2·0 p.p.m. Composites of these contain an average of 0·6 p.p.m. Mo in the silicate phase, 8·0 p.p.m. in the metal phase, and 5·7 p.p.m. in the sulphide phase. The Canyon Diablo and Henbury irons showed 17 and 10 p.p.m. Mo respectively. The siderophilic and chalcophilic characters of molybdenum are similar, and much stronger than the lithophilic. The concentration of molybdenum in the silicate phase of chondrites is substantially the same as in ultramafic rocks.

Silicic and mafic rocks differ but little in molybdenum content as shown by the averages: granitic rocks, 1·1 p.p.m. Mo (based on 135 samples); basalts and diabases, 1·1 p.p.m. (38 samples); gabbros, 0·6 p.p.m. (21 samples); ultramafic rocks, including 9 serpentines, 0·4 p.p.m. (23 samples). Ultramafic rocks are a little lower than other types in molybdenum. An average value of $1 \pm 0{\cdot}5$ p.p.m. Mo may be assigned to the crustal rocks.

The rather uniform distribution of molybdenum among the common igneous rocks is largely due to its ability to replace a number of elements in the lattices of rock-forming minerals. It is found in the feldspars, femic minerals (biotite, amphibole, pyroxene), and, especially, in magnetite and ilmenite, but is not present in significant amounts in quartz. Substitution of molybdenum for ferric iron, titanium, aluminium, and possibly silicon is indicated. These substitutions are in general accord with the ionic radii of the elements involved.

In mafic rocks molybdenum tends to vary with titanium. This relation is well shown in the basaltic flows of upper Michigan. It does not hold for differentiates of certain intrusives (Mt. Bohemia gabbro of Michigan, Endion Sill at Duluth, and probably the main mass of the Duluth gabbro) in which concentration of the alkalies can take place. Molybdenum is markedly enriched in the silicic or alkalic differentiates of mafic magmas, as shown by its concentration in the granophyric red rock phase of the Duluth gabbro and of the Endion Sill. It occurs in greater than average amounts in rocks of alkalic affinities, as shown by syenites, trachytes and some basalts of West Texas, and is doubtless to be classed among the elements concentrated in alkalic differentiation.

In granitic rocks molybdenum appears to be a little less abundant (on the weight basis) than tungsten. Comparative data are not available for mafic and ultramafic rocks.

Shales poor in organic matter contain about as much molybdenum as igneous rocks (average about 1 p.p.m.). Carbonaceous and pyritic shales are likely to be much richer in molybdenum; contents of 100 p.p.m. or more may be encountered. Limestones and dolomites usually contain less than 0·5 p.p.m. Mo except when organic matter is present. Because of the variable amounts of molybdenum in shales it is difficult to arrive at an average value for molybdenum in sedimentary rocks. The content may be appreciably higher than in igneous rocks because of the escape of molybdenum in hydrothermal solutions and volcanic emanations. Deep sea sediments contain an average of a few parts per million of molybdenum. The few metamorphic rocks studied averaged 0·5 p.p.m. No correlation between Mo content and metamorphic grade was observed.

Because of the sparse existing data on the abundance and distribution of molybdenum, and the contradictory character of some of the results, it was considered worthwhile to investigate the geochemistry of this element in greater detail. Most of the new data pertains to igneous and sedimentary rocks. The distribution of molybdenum among the component minerals of some common igneous rocks has been determined. A number of meteorites, particularly chondrites, have been analyzed, including the metal, sulphide, and silicate phases.

Practically all of the results reported are from the experimental work of one of the writers (P.K.K.).

* Present address, University of Arkansas, Fayetteville, Arkansas.

I. Previous Data

The main facts in our present knowledge of the geochemistry of molybdenum are summarized here. Some further references to earlier work are given below in the discussion of the new data.

Meteorites. The data are meagre. I. and W. Noddack [1] found an average of 2·5 p.p.m. of Mo in the silicate phase of meteorites and 17 p.p.m.in iron-nickel meteorites. Klüver (reported by Goldschmidt [2]) found 9 and 11 p.p.m. Mo in the Mukerop and Coahuila irons. The Noddacks [3] gave 11 ppm Mo as the content in troilite.

Igneous rocks. Early estimates of the molybdenum content of igneous rocks by H. S. Washington, F. W. Clarke, and others have only an historical interest, because they were not based on actual determinations of the element. Except for a questionable value of 0·01% MoO_3 reported for a Hawaiian basalt by Ferguson [4], the earliest quantitative results appear to be those of I. and W. Noddack [3], who determined molybdenum in some half-dozen granites, basalts, and other rocks in connection with an investigation of the geochemistry of rhenium. The method used is not mentioned. The average of 7 samples is 14 p.p.m. Mo, which is much too high in the light of later results.

In 1933, Hevesy and Hobbie [5] determined molybdenum in composite samples, using phenylhydrazine as colorimetric reagent:

	Mo, *p.p.m.*
Igneous rocks (composite of 282 Caledonian and Variscan samples from Central Europe)	15
Gabbros and norites (composite of 67 European samples)	3
Granite, Schwarzwald, Germany	12

In 1943, Sandell and Goldich [6] determined molybdenum colorimetrically in 22 American igneous rocks and obtained the following averages:

	Mo, *p.p.m.*
Silicic rocks (13 samples)	2·5
Minnesota granitic rocks (6)	1·9
Texas granitic rocks, Llano region (7)	3
Minnesota sub-silicic rocks (7)	2

Individual values are tabulated in the original paper.

More recently, some spectrographic values for molybdenum in igneous rocks have been reported by Foldvari [7] (Velence Mountains) and Nockolds and Mitchell [8] (plutonic rocks of western Scotland). Wager and Mitchell [9] have studied spectrographically the distribution of various trace elements in the Skaergaard intrusion of East Greenland, composed of a series of rocks formed by strong fractionation of basic magma. They found 3 p.p.m. Mo in gabbro picrite and 1 p.p.m. in the average acid granophyre of the series; none was found in the middle stage differentiates (sensitivity of method about 1 p.p.m. Mo).

While the present work was in progress, Ishimori [10] published results of his colorimetric molybdenum determinations in Japanese volcanic rocks:

	Mo, *p.p.m.*
Average of 10 basalts	0·9
Average of 15 intermediate volcanic rocks	1·1
Average of 10 liparites	3·0
Olivine basalt	0·5
Hypersthene andesite	1·8
Nepheline basalt	1·7

Minerals of igneous rocks. Nockolds and Mitchell [8] found no molybdenum (sensitivity limit about 1 p.p.m.) in the feldspar, biotite, augite, or apatite of the plutonic Caledonian rocks of Western Scotland. A hypersthene contained 3 p.p.m. Mo and a zircon 15 p.p.m. Sphene from a number of rocks contained from 20 to 40 p.p.m. Mo; two sphenes from early rocks contained no detectable molybdenum. These authors attribute the presence of molybdenum in sphene to replacement of Ti^{+4} (radius 0·68 A) by Mo^{+4} (0·68 A).

Wager and Mitchell [9] separated a number of minerals from the rocks of the Skaergaard intrusion and determined their molybdenum contents: olivine 10 p.p.m., magnetite 3 (one 10) p.p.m., ilmenite 3 p.p.m., pyroxene, 2 and 3 p.p.m. The presence of molybdenum in olivine is not easy to explain; replacement of silicon is a possibility according to the authors. The presence of molybdenum in magnetite-ilmenite had already been shown by Sandell and Goldich [6], who found 13 p.p.m. in a concentrate from northern Minnesota. That molybdenum can enter the magnetite lattice appears probable from the presence of 400 p.p.m. Mo in fumarolic magnetite from Katmai [11].

A Scottish Permo-Carboniferous tholeiite was found to contain 0, 2, 5 and 2 p.p.m. Mo in plagioclase, augite, iron ore, and glass respectively [12].

Sedimentary rocks. Data for molybdenum in sedimentary rocks are largely confined to shales rich in organic matter and sulphides. Many European shales of this type have been shown to be strikingly rich in the element. Schneiderhöhn and others [13] found from 100 to 1500 p.p.m. Mo in German shales, with an average of ~150 p.p.m. Thuringian alum shales contain from 80 to 400 p.p.m. Mo [14]. Swedish alum shales show a range from <100 to about 200 p.p.m. [15, 16]. Values from 10 to almost 500 p.p.m. have been reported for Swiss bituminous sedimentary rocks [17]. A maximum of 0·1% Mo is stated to occur in Carinthian shales [18]. High molybdenum contents in shales from other areas have been reported [19; 20; 21; 22; 23, p. 629].

Molybdenum is markedly enriched in some coals and in petroleum; coal ash has been found to contain as much as 0·05% MoO_3 [24].

Arkansas bauxite contains ~18 p.p.m. Mo, more than the nepheline syenite (~6 p.p.m.) from which it is derived [25]. Manganese minerals of sedimentary origin may contain significant amounts of molybdenum, e.g. 0·005% MoO_3 in psilomelane [26]. Small amounts of molybdenum, e.g. 0·005% MoO_3 in psilomelane [26]. Small amounts of molybdenum are found in some Swedish iron ores, but in most the content lies below the spectrographic sensitivity of 10–30 p.p.m. [27]. Molybdenum sometimes occurs in appreciable amounts in phosphate rock. Robinson 28] found 208 p.p.m. MoO_3 in a Wyoming sample and 62 p.p.m. in an Egyptian sample. However, some phosphate rocks (as the Tennessee) contain only 1 or 2 p.p.m. MoO_3.

Molybdenum has been determined in deep sea deposits and figures are given below.

Metamorphic rocks. Data are very scarce. A Scottish hornfels was found to contain 5 p.p.m. Mo [8]. Very low contents have been reported for three metasomatic-metamorphic rocks of Co. Donegal, Ireland [29].

Sulphide minerals. According to the Noddacks [3], the average value for molybdenum in primary sulphides (pyrrhotites, pyrites, pentlandites, and nickeliferous pyrites) is 20 p.p.m.

II. The Analytical Method

All the determinations of molybdenum were made by a colorimetric (photometric) method. This method is based on the familiar reaction between molybdenum (VI), thiocyanate, and stannous chloride in acid medium to give an amber-coloured molybdenum thiocyanate, probably containing molybdenum in the quinquevalent state. This complex is extractable by various organic solvents (alcohols, ethers, esters). The procedure adopted differs from an earlier one [30] in the use of isopropyl ether in place of ethyl ether as extractant, and photometric measurement of the colour intensity of the extract instead of visual comparison.

In brief, the procedure is carried out as follows. A 0·5 g silicate sample is fused with 3 g of sodium carbonate in platinum. The melt is leached with hot water and the cold filtrate is treated with excess hydrochloric acid (added quite rapidly to prevent precipitation of silica) to make the acidity 1 *M*. The solution, now having a volume of about 75 ml, is treated with 1 ml of 1% ferrous ammonium sulphate, 3 ml. of 10% potassium thiocyanate, and 1·5 ml of 10% stannous chloride in 1 *M* hydrochloric acid. The mixture is extracted with 5 ml of reagent-quality isopropyl ether previously shaken with a little stannous chloride solution. The aqueous phase is discarded and the clear ether layer is run into a 1 cm absorption cell and its transmittancy determined at 460–475 mμ. In the present work a Leitz-Rouy filter photometer with a 460 filter was used. The standard curve is established similarly, with sodium carbonate present. A blank should be run through the whole procedure (with a good grade of sodium carbonate it should not exceed 0·2 p.p.m. Mo based on the sample). No element in the amounts likely to be found in igneous rocks interferes. The faint colouration given by tungsten is about 1% as strong as that given by an equal weight of molybdenum. Since these elements occur in comparable amounts in igneous rocks, the effect of tungsten rarely needs to be considered. The precision of the method is estimated to correspond to 0·1–0·2 p.p.m. average deviation for 0–1 p.p.m. Mo (0·5 g sample); above 1–2 p.p.m. Mo, it is $\sim \pm 10\%$. There is no distinct tendency toward either high or low results.

Results obtained by the above procedure were checked by another method [31], in which molybdenum is isolated as sulphide by coprecipitation with Sb_2S_5 before photometric determination. In the latter method, elements such as tungsten, vanadium, uranium, niobium, tantalum, and phosphorus, as well as many others, remain in solution. Some half-dozen silicic and sub-silicic igneous rocks gave identical results by the two methods, thus making likely the absence of unsuspected errors in the more rapid direct extraction method, which was therefore applied in most of the subsequent work.

The emission spectrographic procedures lately applied in the determination of molybdenum in silicate rocks appear to have a sensitivity of about 1 p.p.m. Mo and are thus about one-fifth as sensitive as the present colorimetric method. Because of its poor sensitivity the spectrographic method in its present form is inadequate for tracing molybdenum in igneous rocks, which, as will be shown, have average contents of $\sim$1 p.p.m. Mo. Even with larger amounts of molybdenum the precision of the spectrographic determination is inferior to that of the colorimetric method. The relatively large sample required in the colorimetric method is no disadvantage when rocks are being analyzed. On the other hand the spectrographic method, with a sample size of some milligrams, has the advantage when the component minerals of a rock are to be analyzed, provided the molybdenum content is greater than 1 p.p.m.

No significant amount of molybdenum was introduced into crushed rock samples from the steel mortar. Quartz crystal crushed under the same conditions showed no molybdenum on analysis. The maximum effect of any introduced molybdenum-bearing steel particles would be shown in the strongly magnetic bromoform-heavy fraction of the separated minerals of a rock, but since magnetite normally contains relatively much molybdenum (as shown by samples

not crushed in steel) such contamination is not likely to be serious. Probably less than 0·05% steel will be introduced from the steel mortar [32]; if the steel contains 0·01% Mo (higher than the average), 0·05 p.p.m. would be added to the molybdenum content of the sample. This is a negligible amount, although if concentrated in 1% of the sample, that fraction would show 5 p.p.m. too much Mo.

III. Molybdenum in Rocks and Minerals

A. Igneous rocks and their component minerals

Table 1 contains the results of the determination of molybdenum in composites of igneous rocks (prepared by mixing equal weights of the individual samples). The tables following (2–7) give the molybdenum contents of individual igneous samples grouped according to rock type and area. Except for the African granites and some mafic rocks, the individually analyzed samples are not represented in the composites of Table 1. The molybdenum contents of a number of series of closely related rocks are given below under "Discussion."

The literature references in these tables furnish information on the petrography, chemistry, or geological setting of the samples analyzed or of similar rocks of the area.

Table 1. *Igneous composites*

Silica Range %	*Average* SiO_2, %	*Rock Type and Number of Samples*	*Region*	Mo, *p.p.m.*	W, *p.p.m.*	Mo/W
80·6–76·3	77·7	Granite (12)	U.S.A.	0·9	2·0	0·4
81·5–75·1	77·0	Granite (8)	U.S.A. and Canada	0·8		
77·4–71·5	74·1	Granite, etc. (9)[a]	California	0·8, 0·8	1·4	0·6
74·3–70·6	72·6	Granite (7)	Canada	3·8, 3·7[b]	1·4	2·7
		Granite (8)[c]	Canada	3·4		
73·9–70·0	72·0	Granite (9)	Africa	0·6	1·3	0·5
69·6–65·5	68·4	Granitic (14)[d]	Various[e]	0·9	1·3	0·7
—	—	Granite-gneiss (14)	Canada, etc.	0·5		
62·9–62·1	62·6	Diorite (3)	California	0·9, 0·8	1·2	0·7
64·1–56·0	60·3	Syenite (6)	N.Y. and Minn.	0·8	1·9	0·4
57·9–49·6	53·1	Phonolite (4)	Africa	1·5		
	47·6	Gabbro-diorite (4)	California	0·8		
57·7–44·4	50·0	Mafic (24)[f]	Various[g]	0·7		
54·7–33·4	42·8	Ultramafic (6)[h]	U.S.A. and Newfoundland	0·4		

[a] 4 granites, 2 quartz monzonites, 1 monzonite, 2 granodiorites.

[b] Mo isolated by sulphide precipitation.

[c] Same as the preceding composite except for an additional sample.

[d] 6 granites, 1 granite porphyry, 1 felsite porphyry, 1 porphyry, 1 quartz monzonite, 1 granodiorite, 1 diorite, 2 dacites.

[e] Canada 2, New York 1, Texas 2, Montana 2, Wyoming 1, California 2, 4 from unspecified U.S.A. or Canadian localities.

[f] 9 gabbros, 1 norite, 4 diabases, 8 basalts, 1 periodtite, 1 pyroxenite. 11 of these samples were analyzed separately (avg. 0·8 p.p.m. Mo) and the values reported in the other tables.

[g] Eastern and western U.S.A. 13, Newfoundland 1, Africa 1, Antarctica 3, India 1, unspecified localities probably U.S.A.) 5.

[h] 1 peridotite, 1 dunite, 2 harzburgites, 1 bronzitite, 1 pyroxenite.

Table 2. Molybdenum in silicic volcanic rocks

Sample	Mo, *p.p.m.*
Felsite, Bare Hill, Michigan (probably intrusive) [33, No. 3156]	1·1
Felsite, Mt. Houghton, Mich., upper half [33, No. 3158]	1·4
Felsite, Mt. Houghton, Mich., lower half [33, No. 3157]	0·8
Rhyolite, Cook Co., Minn.	3·2
Rhyolite porphyry, Great Palisades, Lake Co., Minn.	1·5
Rhyolite, overlying Endion Sill, Duluth, Minn. [34, Table 1, No. 7]	1·5
Rhyolite (intrusive), Iron Mtn., Mo.	3·4
Rhyolite, Skrainka, Mo.	3·4
Soda rhyolite (intrusive). West Texas	4·3
Rhyolite, White Pine, Nev.	1·6
Rhyolite, West Indies	0·6
Liparite, Ishikawa Prefecture, Japan	0·8
Liparite, Nishiyama, Yamagata Pref., Japan	0·8
GLASSES	
Obsidian (black), Obsidian Cliff, Yellowstone Park	4·0
Rhyolitic obsidian, Clear Lake, Calif. [35, No. 13]	0·3
Biotite rhyolitic pumice, Clear Lake, Calif. [35, No. 11]	0·2
Twelve volcanic glasses from Arizona and New Mexico	2·6, 3·8, 2·7, 3·8, 2·7, 2·7, 2·0, 5·0, 4·4, 4·1, 1·5, 2·5 (avg. 3·2)[a]
Perlite, Washington State	1·2
Perlite, Nagano Pref., Japan	1·4
Pitchstone, Nagano Pref., Japan	0·9

[a] An associated felsite contained 0·8 p.p.m. Mo.

Table 3. Molybdenum in granitic rocks

Sample	Mo, *p.p.m.*
MINNESOTA	
Middle Keweenawan	
Hornblende granite ("St. Cloud Red"), Stearns Co. [36, p. 1005]	1·4, 1·5, 1·3
Quartz monzonite, Rockville, Stearns Co. [37]; [36, p. 1006]	1·5
Granite ("Mottled Venetian"), Stearns Co.	0·9
Porphyritic granite, Stearns Co.	3·0
Porphyritic granite, Stearns Co.	1·1
Biotite granite, coarse-grained, Benton Co.	1·2
Biotite granite, fine-grained, Benton Co.	0·9
Granite, red, Benton Co.	1·8
Granite porphyry, Benton Co. [36, p. 1003]	0·9
Quartz latite porphyry [36, p. 1008]	0·9
Aplite, Stearns Co.	0·7
Algoman	
Granodiorite, St. Cloud area [36, p. 1012]	2·0
Granodiorite, Sherburne Co.	1·7
Granodiorite, Stearns Co.	2·5
Granodiorite (?), Watab [38, p. 38]	0·5
Granite porphyry, Sauk Rapids [38, p. 39]	0·7, 0·5
Quartz monzonite (Warman), near Pierz [38, p. 34]	1·7
Quartz monzonite (Warman), northern Kanabec Co.	0·5
Quartz monzonite, abandoned quarry, Warman [36, p. 1011]	0·2
Granite, Lover Falls, Snake River Kanabec Co. [38, p. 44]	0·4
Granite-gneiss (McGrath gneiss), Southern Aitkin Co. [36, p. 1014]; [6, p. 110, No. 3]	0·5
Granite, Giants Range, near Virginia	0·2, 0·3
Hornblende granite, 6 miles S.S.E. of Ely	0·3, 0·2
Granite, Vermilion batholith, Slim Lake	0·4
Meta granite, near Chisholm	1·2
Granite-gneiss, Morton (unclassified pre-Cambrian) [40, p. 22, No. 1]	0·1
Avg.	1·0
OTHER U.S.A. LOCALITIES	
Granite, Chippewa Falls, Wis.	0·2, 0·1
Granite, Westerly, R. I. (standard granite G-1, [39])	6·5, 6·7
Granite, Chelmsford, Mass.	1·8
Hornblende granite, Devil's Slide, Percy Quadrangle, N.H. [6, p. 114]	1·1, 0·9
Granite, Holladay Mtn., Mo.	3·8
Granite, Holladay Mtn., Mo.	0·9
Granite, Holladay Mtn., Mo.	2·2
Granite, dike, Skrainka, Mo.	0·5
Granite, Mine LaMotte, Mo.	0·7
Granite, Front Range, Colo.	0·8
Quartz monzonite, Boulder Co., Colo.	0·5
Granite, Mt. Rubidoux, Calif.	2·5
Granite, Mt. Stanford, Calif.	0·7
Avg.	1·7
JAPAN	
Granite, Masutomi, Yamanashi Prefecture	0·8
Granite, Naegi, Gifu Pref.	0·7
Biotite granite, Okayama Pref.	0·7
Biotite granite, Nagano Pref.	0·7
Biotite granite, Gifu Pref.	0·4
Biotite granite, Yamanoo, Ibaragi Pref.	0·4
Hornblende granite, Gifu Prof.	0·4
Hornblende granite, Samekawa, Fukushima Pref.	0·7
Avg.	0·6
CHINA	
Granite	0·7
AFRICA [41]	
Granite, Pietersburg, Transvaal	0·2
Granite, Pietersburg, Transvaal	0·4
Granite, Pretoria-Johannesburg batholith	0·2
Granite, Swaziland	0·7
Granite, Port Shepstone, Natal	0·8
Granite, Matapos, southern Rhodesia	0·6
Granite, Mitoko, southern Rhodesia	0·6
Granite, southern Rhodesia	0·5
Granite, Mutondo, nothern Rhodesia	0·7
Avg.	0·5
ANTARCTICA	
Granite	1·2
Granite	0·4
Granodiorite	0·5
Granodiorite	0·5
Avg. of all values = 1·0 p.p.m.	

Table 4. Molybdenum in intermediate rocks

Sample	Mo, *p.p.m.*	*Sample*	Mo, *p.p.m.*
U.S.A.		*WEST INDIES*	
Hornblende tonalite, Freedhem, Minn. [36, p. 1010]	0·7	Andesite	0·2
		Andesite	0·7
		Porphyritic dacite	1·2
Melagranodiorite, Watab, Minn. [36, p. 1013]	1·1	Quartz diorite	0·2
		Diorite	0·2
Augite andesite, Clear Lake area, Calif. [35, No. 2]	0·5		
		JAPAN	
Olivine andesite, Clear Lake, Calif. [35, No. 3]	0·2	Augite andesite, Kumamoto Pref.	1·2
Pyroxene rhyodacite, Clear Lake, Calif. [35, No. 6]	0·4	Augite andesite, Suwa, Nagano Pref.	0·7
Olivine dacite, Clear Lake, Calif. [35, No. 7]	0·5	Pyroxene andesite, Yutanaka, Nagano Pref.	0·4
Hypersthene dacite, Clear Lake, Calif. [35, No. 8]	0·0	Pyroxene andesite, Yakedake, Nagano Pref.	1·2
Biotite hornblende rhyodacite, Clear Lake, Calif. [35, No. 9]	0·3	Hornblende biotite andesite, Gifu Pref.	1·5
Silicic pyroxene dacite, Clear Lake, Calif. [35, No. 10]	0·4	Diorite, Yamanashi Pref.	1·2
Dacite, San Luis Obispo Co., Calif.	0·6	Diorite, Ishikawa, Fukushima Pref.	0·4
Diorite, unknown locality	0·2	Gabbro diorite, Gifu Pref.	0·8
Diorite, unknown locality	1·2	Gabbro diorite, Minano, Saitama Pref.	0·4
Avg.	0·5	Avg.	0·9
MEXICO		*PALAU ISLANDS*	
Taqui flow, Paricutin	1·2	Dacite	0·1
Zapico flow, Paricutin	1·2	Average of all values = 0·7 p.p.m.	

Table 5. Molybdenum in basalts and diabases

	Mo, *p.p.m.*		Mo, *p.p.m.*
MINNESOTA		Diabase, Fairfax Co., Va. (standard diabase W-1 [39])	(0·8), 0·5, 0·4, 0·5
Diabase, Taylors Falls	0·7	Diabase, Va	0·7
Diabase, Taylors Falls	0·7	Picritic basalt, Terlingua-Solitario, Texas	1·4
Diabase, Taylors Falls	0·5	Basalt porphyry, West Texas	3·1
Basalt, dike in granodiorite, St. Cloud [36, p. 1004]	0·8	Ultrabasic basalt, West Texas	1·3
Diabase, near Beaver Bay [42, p. 35, No. 1]	1·2	Olivine basalt, Jefferson Co., Colo.	1·6
		Basalt, Idaho	1·8
Diabase gabbro, near Beaver Bay [42, p. 35, No. 2]	1·0	Olivine basalt, Oreg.	1·0
		Olivine basalt, Oreg.	1·0
Olivine diabase, near Beaver Bay [42, p. 35, No. 3]	1·0	Olivine basalt, Oreg.	0·6
		Olivine basalt, Oreg.	0·8
Diabase, bluff opposite Encampment Island, Lake Co. [40, p. 46]	0·5	Olivine basalt, Oreg.	0·6
		Olivine basalt, Oreg.	0·6
Diabase, Grand Marais, barrier of harbour [6, p. 110]	1·4, 1·4, 1·5	Olivine basalt, Oreg.	0·6
Basalt, Cook Co.	0·2	Olivine basalt, Clear Lake, Calif. [35, No. 1]	0·8
Diabase, 3 mi. N.E. of Grand Marais	1·4	Basalt, unknown U.S.A. locality	1·2
Porphyritic diabase or basalt, Cook Co. (contains visible pyrite)	7·3, 7·0	Avg.	1·1
Greenstone, Winton	0·5		
Greenstone, near Ely	0·4		
Greenstone, near Ely	0·2, 0·2	*LOCALITIES OUTSIDE U.S.A.*	
Avg.	0·8 (*Omitting Cook Co. diabase*)	Diabase, Kotaki Village, Nishikubiki Co., Niigata Pref. Japan	0·5
		Diabase, Gifu Pref. Japan	2·0
		Trap, Deccan	1·2
		Olivine basalt, Palau Islands	0·5
MICHIGAN (See Table 9)		Basalt, Antarctica	0·7
		Diabase, Antarctica	0·8
OTHER U.S.A. LOCALITIES		Avg.	1·0
Diabase, Conn.	1·0	Average of all	1·1

Table 6. Molybdenum in gabbros and related rocks

	Mo, *p.p.m.*		Mo, *p.p.m.*
Gabbro, Duluth, Minn., above cement plant	0·8, 1·0	Norite, Essex Co., N.Y.	0·2
Gabbro, Duluth, Lookout Point	0·4	Gabbro, Charlottesville, Va.	1·0
Gabbro, Duluth, Fairmount Park	0·8	Olivine gabbro, Cripple Creek, Colo.	0·5
Orthoclase gabbro, Duluth	1·5	Gabbro-diorite, Gifu Prefecture, Japan	0·8
Gabbro, near Ely, Minn. (contains Cu-Ni sulphides)	0·6	Gabbro-diorite, Minano, Saitama Pref., Japan	0·4
Gabbro anorthosite, Lake Isabella, Minn.	0·5	Gabbro, No. Transvaal, Africa	0·5, 0·4
Anorthosite, Split Rock, Minn. [42, p. 55]	0·5	Gabbro, Great Dyke, Africa	0·1
Anorthosite, Crystal Bay, Minn.	0·1	Gabbro, Bushveld Complex, Africa	0·5
Hornblende gabbro, Little Falls, Minn. [36, p. 1010]; [6, p. 110]	0·9, 0·9, 0·8	Gabbro, S.E. Bushveld Complex, Africa	1·1
Hornblende norite, Stearns Co., Minn. [36,] p. 1009]	0·2	Gabbro, Antarctica	0·2
Hornblende norite (?), probably hornfels, Stearns Co., Minn. [36, p. 1009]	1·2	Avg.	0·6

Table 7. Molybdenum in ultramafic rocks

	Mo, *p.p.m.*		Mo, *p.p.m.*
Pyroxenite, Lewis Hills, Newfoundland	0·6	Serpentine, San Francisco, Calif.	0·0
Peridotite, Syracuse, N.Y.	0·8	Serpentine, U.S.A., localoty unknown	0·6
Peridotite, Euclid, N.Y.	1·3	Serpentine, Gifu Prefecture, Japan	0·4
Peridotite, locality unknown	0·5	Serpentine, Yorii, Saitama Pref., Japan	0·4
Dunite, N.C.	0·3, 0·5	Serpentine, Miyamori, Iwate Pref., Japan	0·4
Dunite, Balsam, N.C.	0·0	Antigorite, unknown locality	0·1
Serpentinized dunite, Venezuela	0·4	Kimberlite, So. Africa	0·9
Serpentine, Hoboken, N.J.	0·0	Avg.	0·4
Serpentine, Yearlying Head, Llano Region, Texas	0·1		
Serpentine, Gillespie Co., Texas	0·2, 0·2		

Molybdenum in the component minerals of some igneous rocks. The minerals were separated by hand picking, by bromoform flotation, and magnetically. From 0.2 to 0.5 g samples were used for the molybdenum determination. The results are recorded in Table 8.

Table 8. Molybdenum in component minerals of some igneous rocks

Rock	*Mineral*	*Percentage of rock*	Mo *in mineral p.p.m.*	*p.p.m.* Mo *contributed to rock*	Mo *in rock by direct analysis p.p.m.*
Quartz monzonite, Rockville, Minn. (For description of rock see [36] and [37])	Microcline	35	0·4	0·15	1·5
	Plagioclase (An 28)	35	2·5	0·9	
	Biotite[a]	7	3·1	0·2	
	Quartz	—	0·1	0·0	
				1·25 total	
Hornblende granite, Stearns Co., Minn.	K-feldspar	68	0·9	0·6	1·3, 1·4
	Plagioclase	15	0·3	0·05	
	Hornblende + biotite	7	8·7	0·6	
	Quartz	10	0·0	0·0	
				1·3 total	
Granite, Devils Slide, N.H. [6, p. 114]	Feldspar (chiefly perthite)	70	(1·3)[b]	0·9	1·0
	Amphibole (sodic)	5	1·8	0·1	
	Quartz	25	(0·0)	(0·0)	
				1·0 total	
Granodiorite, St. Cloud, Minn. [37]	Feldspar	87	1·7	1·5	2·5
	Heavy non-magnetic fraction (chiefly hornblende)	11	4·3	0·5	
	Magnetite	2	30	0·6	
				2·6 total	
Hornblende tonalite, Freedhem, Minn. [37]	Feldspar	50	0·5	0·25	0·7
	Heavy fraction (mostly hornblende and biotite)	50	1·2	0·6	
				0·85 total	
Augite-syenite (field name), Cook Co., Minn.	Light fraction (mostly feldspar)	73	1·2	0·8	3·8
	Non-magnetic heavy fraction (pyroxene, amphibole, ilmenite, epidote)	~20	4·3	0·9	
	Magnetic fraction	~ 7	37	2·6	
				4·3 total	
Gabbro, Duluth, near Bardon's Peak	Plagioclase	~80	0·4	0·3	0·9
	Non-magnetic heavy fraction (about one-half amphibole, remainder epidote, pyroxene, ilmenite-magnetite, etc.)	~18	1·6	0·3	
	Magnetite (and intergrown ilmenite)	2·5	16	0·4	
				1·0 total	
Gabbro, Duluth, Fairmount Park	Plagioclase	80–85	0·6	0·5	0·8
	Non-magnetic heavy fraction (mostly pyroxene, some ilmenite-magnetite, etc.)	15–20	1·6	0·3	
	Magnetite (and intergrown ilmenite)	1	(15)[c]	(0·15)	
				~1·0 total	

[a] Includes about 1 per cent hornblende and traces of zircon and apatite.
[b] By difference, assuming Mo content of quartz less than 0·2 p.p.m.
[c] Mo content of magnetic fraction not determined but assumed to be about the same as in the preceding gabbro.

For reference, the molybdenum contents of some miscellaneous silicate minerals are given here:

	Mo, *p.p.m.*
Feldspar from ordinary pegmatite, Kanabec Co., Minn.	0·4
Feldspar from vein in granite, Kanabec Co., Minn.	0·2
Pink pegmatite, mostly feldspar, Snake River, Kanabec Co., Minn.	0·1
Pegmatitic feldspar, unknown locality	0·5
K-feldspar, from pegmatite, unknown locality	0·2
Amazonite, Amelia Court House, Va.	0·0
Amazonite, Kragorö, Norway	0·0
Amazonite, Mont Anpanobe, Madagascar	0·0
Quartz from vein in granite, Kanabec Co., Minn.	0·1
Quartz, crystal, unknown locality	0·0
Magnetite, from pegmatitic streak in granite, Freedhem, Minn.	15
Enstatite, Webster, N.C.	0·0
Hypersthene, Nain, Labrador	0·1
Hypersthene, from basalt flow, West Texas	0·4, 0·5
Diopside, near Hull, Quebec	0·2
Diallage, Sonoma Co., Calif.	0·1
Pyroxene, Zonolite Mtn., Libby, Mont.	0·1
Amphibole, Salem district India (from anorthite-hornblende gneiss)	0·0
Amphibole, Salem district India (from chromite amphibolite)	0·0
Glaucophane, Mendocino Co., Calif.	0·3

Discussion

General. The frequency distribution of molybdenum in granitic, mafic and ultramafic rocks is shown in Fig. 1. The amounts and the distribution patterns are strikingly similar for felsic and mafic rocks.

We have the following averages:

	Mo, *p.p.m.*
Granitic rocks	
From weighted average of 7 composites (Table 1) based on 74 samples	1·1
From 61 individual analyses (Table 3)	1·0
Intermediate rocks (Table 4), 29 samples	0·7
Basalts and diabases (Table 5), 37 samples	1·0
Gabbros (Table 6), 21 samples	0·6
Mafic (Table 1), 24 samples	0·7
Ultramafic (Table 1 and 7), 23 samples (including 9 serpentines)	0·4

The rounded value 1 p.p.m. may be assigned as the average molybdenum content of granitic rocks and also of basalts and diabases. The average for common intermediate rocks may also be rounded off to 1 p.p.m. The average for gabbros may be given as 0·5 ± p.p.m., but is quite uncertain. Ultramafic rocks (including serpentines) have a lower molybdenum content than the felsic and mafic; the present results indicate an average of 0·5 p.p.m. or less, but this is based on only 23 samples. Since the abundant rocks have very similar amounts of molybdenum, the

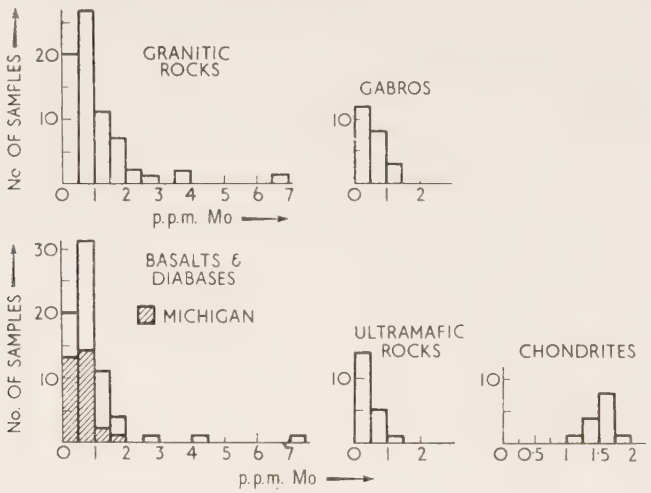

Fig. 1. Frequency distribution on molybdenum in various rock types and in chondrites.

average for the lithosphere is likely to be near 1 p.p.m. Mo; an average falling outside the limits 0·5–2 p.p.m. seems unlikely. Hevesy and Hobbie's [5] averages for molybdenum in igneous rocks are doubtless much too high, especially their figure of 15 p.p.m. for granites. Of some 60 granitic rocks individually analyzed by us, only one showed a molybdenum content as high as 7 p.p.m., and the next highest was 3·8 p.p.m.

Our results are in good agreement with Ishimori's averages for basaltic and intermediate Japanese volcanic rocks (each about 1 p.p.m.). There is some indication from Table 2 that silicic volcanic rocks tend to run somewhat higher than basaltic rocks in molybdenum. Some support for this belief is lent by results of Patterson [43], who found 7 and 10 p.p.m. Mo in a rhyolite and obsidian of northeast Ireland, compared to 1 p.p.m. or less in associated Tertiary olivine and tholeiitic basalts. Further, the data of Ishimori already quoted show more molybdenum in Japanese liparites than in basalts and intermediate volcanic rocks. In passing, it may be noted that there is no evidence for any essential difference in the molybdenum contents of pre-Cambrian and Tertiary or Recent volcanics.

More exact averages will require analysis of a larger number of samples. Since the present results show that the range of variation of molybdenum in the common igneous rocks is moderate, further work on abundance could perhaps be based on small composites from well-scattered areas of the globe. The so-called regional factor may play some role in the distribution of molybdenum. Thus the upper Michigan basic lavas seem to be a little poorer in molybdenum than similar rocks

from Minnesota and elsewhere. The African granites (Table 3) tend to be lower than similar granites of other regions. On the whole, however, uniformity predominates. The high molybdenum content of the Canadian granite composite (Table 1) may be due to the presence of molybdenite in one of the component samples.

Oceanic basalts are very poorly represented in our analytical material, and the basaltic average is uncertain to the extent that the molybdenum contents of oceanic and continental basalts may differ.

Although rocks of different types differ but little in average molybdenum content, individual rocks of any one type show a considerable, but not excessive, distributional spread of values. Granitic, intermediate, basaltic, and gabbroic rocks rarely contain less than 0·2 p.p.m. Mo or more than 5 p.p.m. The great majority of values accordingly fall in the range (1/5 × mean) to (5 × mean). As a matter of fact, of some 150 samples of the abundant types mentioned (Tables 3–6), slightly less than 10% fall outside the limits 0·2–2 p.p.m., or a ten-fold range of variation. Samples with molybdenum contents outside this range may be called unusual in greater or less degree.

The percentage of samples from the tables mentioned having molybdenum contents greater than 1·0 p.p.m. are as follows: granitic rocks (61 samples), 28; intermediate rocks (29 samples), 31; basalts (including Michigan basalts of Table 9, 67 samples in all), 21; gabbros (21 samples), 14; ultramafic rocks (17 samples), 6.

Manner of occurrence of molybdenum in igneous rocks. Molybdenum does not closely follow any single major constituent of igneous rocks and thus differs from manganese, nickel, cobalt, zinc, gallium, and various other minor or trace elements whose distribution is governed principally by one of the major constituents. The analyses of the component minerals of common igneous rocks show that molybdenum can occur in important quantities in alkali and plagioclase feldspars, pyroxene, amphibole, biotite, and, especially, magnetite-ilmenite. These facts are, in the main, explained by the substitution of Mo for Al^{+3}, Fe^{+3} and Ti^{+4} in mineral lattices, and are in general accord with the ionic radii of the elements involved[1]:

Goldschmidt *ionic radii*, Å		Ahrens *ionic radii*, Å	
Be	0·34	Be	0·35
Si	0·39	Si	0·42
Al	0·57	Al	0·51
V(+4)	0·61	Mo(+6)	0·62
Ti(+4)	0·64	V(+4)	0·63
V(+3)	0·65	Fe(+3)	0·64
Fe(+3)	0·67	Mg	0·66
Mo(+4)	0·68	Ti(+4)	0·68
Mg	0·78	Mo(+4)	0·70
Fe(+2)	0·83	V(+3)	0·74
		Fe(+2)	0·74

[1] The valency of molybdenum in igneous rocks and magmas is uncertain. From analogy with MoS_2, it is generally assumed that molybdenum is usually quadrivalent in silicates. Other valences (+3, +5) may be possible. Because of the low oxidation potential of most magmas the hexavalent state is unlikely. The difficulty of the valence state is mitigated by the similarity in the ionic radii of +4, +5 and +6 molybdenum, the difference between +4 and +6 being only 0·08 Å according to Ahrens [44].

From the high molybdenum content of magnetite and ilmenite, compared to other common rock-forming minerals, substitution of Mo for Fe^{+3} and Ti^{+4} and possibly Fe^{++} may be inferred. Because of the low molybdenum contents of ultramafic rocks the tendency for Mo to replace Mg^{++} and Fe^{++} would seem to be subordinate to the tendency to replace Fe^{+3} and Ti^{+4}. On the basis of ionic radii alone, substitution of Mo for Mg^{++} and Fe^{++} would not appear impossible. However, Wager and Mitchell [9] were inclined to explain the occurrence of appreciable amounts of molybdenum in the ferriferous olivines of the Skaergaard rocks by replacement of silicon rather than of ferrous iron or magnesium. One would expect molybdenum to prefer the role of anion to that of cation. The great difference in ionic radii between Mo^{+4} and Si is a difficulty, however.

Molybdenum is almost certainly present in the crystal structure of feldspars, both the potassium and plagioclase feldspars (Table 8). Substitution of molybdenum for aluminum or silicon or both are possibilities. From the standpoint of ionic sizes, substitution for aluminum would be expected to predominate. Besides, the general distribution pattern of molybdenum in ingenous rocks does not seem to point to any close relation between it and silicon. The balancing of charges in the feldspars (and other minerals) can be effected by various co-substitutions and entails no difficulties.

No significant quantity of molybdenum is found in quartz, of various origins (igneous, pegmatitic, vein) if the present results can be taken as representative.

In some granitic rocks more than one-half of the total molybdenum is accounted for by the feldspars, as Table 8 shows. At least in some granitic rocks, biotite and amphibole do not contain any striking amounts of molybdenum, e.g. about 3 p.p.m. in the biotite of the Rockville, Minn., quartz monzonite and 1·8 p.p.m. in the amphibole of a New Hampshire granite. However, these amounts are higher than the usual amounts in feldspars. The heavy non-magnetic fraction of the St. Cloud, Minn., granodiorite, consisting mostly of hornblende, contains about 4 p.p.m. Mo. The hornblende and biotite of a hornblende granite from Stearns Co., Minn., showed even more molybdenum (8·7 p.p.m.) but some magnetite may have been present in this fraction. Molybdenite occurs in granites at times, and two or three anomalously high results obtained in the present work may be due to the presence of this mineral.

Small amounts of molybdenum occur in the feldspars of ordinary pegmatites in granitic rocks, but the impression is obtained that the values are smaller (at least not greater) than those for the feldspars of granitic rocks. Amazonite appears to be very low in molybdenum.

Among the common minerals of mafic rocks, magnetite-ilmenite has the highest molybdenum content, and its contribution to the total may be considerable in spite of its relatively small amount. The concentration of molybdenum in pyroxene of gabbros—if the Duluth gabbro can be taken as representative—is not great (1 to 2 p.p.m.). The plagioclase of the Duluth gabbro contains about 0·5 p.p.m. Mo and it may account for one-third or one-half of the total molybdenum in the rock. Some plagioclase, as in anorthosite, may contain less molybdenum than this, as shown by the figure 0·1 p.p.m. obtained for an anorthosite listed in Table 6.

The appreciable amount of molybdenum in sphene and zircon [8] is probably a result of the close similarity in the ionic sizes of Mo, Ti and Zr.

If it could be written, the expression for the molybdenum content of an igneous rock would contain many terms, with more or less variable co-efficients, and only when one of the terms has a value greater than the rest can we describe the distribution of the element with a measure of success. In mafic rocks, especially basalts and diabases, titanium is to some extent an index element for molybdenum. The relationship between the two elements is well shown by the basic lavas of upper Michigan, considered in more detail below (Fig. 2). But even in mafic rocks of different regions, a certain correspondence is evident (Fig. 3), especially at lower molybdenum contents. This does not mean that the relation is entirely a direct one. It is partly accounted for by the replacement of titanium by molybdenum in ilmenite and of ferric iron in magnetite, which in amount runs more or less parallel to ilmenite. Besides, molybdenum may be expected to enter other minerals in somewhat the same proportion that Ti^{++++} and Fe^{+++} do. Even if there were no substitution of molybdenum for these elements, some correlation would result from their inability to enter the early crystallizing minerals, such as olivine.

In granitic rocks, molybdenum and titanium part company, much or most of the molybdenum entering the feldspars as already noted. Because of the variability of the molybdenum content of granites of about the same chemical composition, we have made no serious attempt to correlate molybdenum with other constituents in these rocks. The amount in apparently normal granites may vary from the limit of detectability ($\sim$0·1 p.p.m.) to 2 or 3 p.p.m., rarely more. When the problem of the origin of granites has been solved, it may be possible to explain such differences. The granite-gneisses (composite in Table 1) show average or less than average molybdenum contents. In some granitic rocks, as those of the Llano region of Texas, the molybdenum content mounts with silica and increasing differentiation. At a late stage in crystallization differentiation when hydrogen sulphide has attained a notable concentration, the molybdenum that has escaped incorporation in oxide and silicate minerals may be precipitated as molybdenite, and some may even reach the surface in magmatic waters or emanations. However, the amounts in silicate and oxide minerals of igneous rocks must be incomparably greater than that in the other forms.

Molybdenum is to be counted among the elements concentrated in alkalic differentiation. The phonolite composite of Table 1 contains almost twice as much molybdenum as the typical granites. Nepheline syenite from Hot Springs, Ark., contained 3·5 p.p.m. Mo. Other examples are given below.

In subsilicate rocks, molybdenum shows a distributional resemblance to vanadium, which (possibly as V^{+4}, 0·61A according to Goldschmidt) substitutes for Fe^{+3} and Ti^{+4}. Both are characteristic of magnetite-ilmenite. Vanadium differs from molybdenum in being present in much smaller amounts in silicic than in subsilicic rocks. This is partly explained by the reluctance of vanadium to enter the feldspar structure; it shows little tendency to replace aluminium (or silicon).

Molybdenum resembles beryllium in avoiding ultramafic rocks, although this tendency is more pronounced for beryllium. A decided preference for silicic rocks, as compared to subsilicic (basalt, diabase, gabbro), is shown by beryllium, whereas

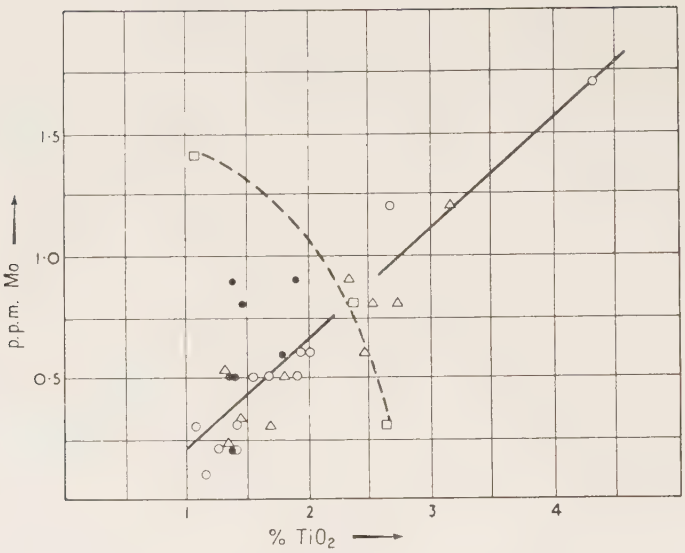

Fig. 2. Mo vs. TiO_2 in Michigan Keweenawan rocks
o Greenstone flow.
• Kearsarge flow.
△ Miscellaneous basic flows.
▫ Mt. Bohemia intrusive (gabbro, aplite, intermediate gabbro, basic gabbro).

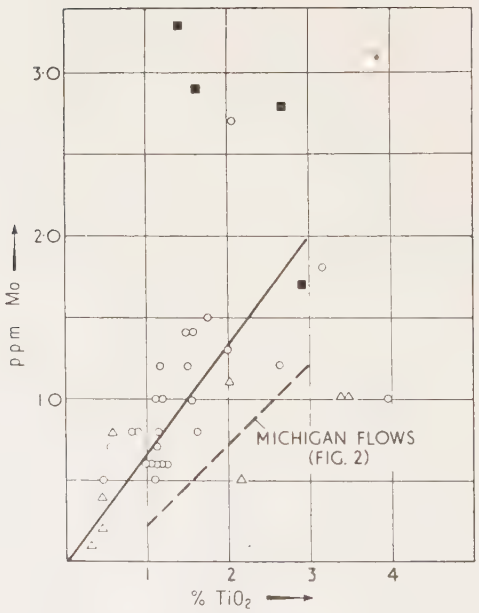

Fig. 3. Mo vs. TiO_2 in mafic rocks (U.S.A., Africa, Antarctica, etc.)
o Basalt and diabase.
△ Gabbro.
■ Endion Sill samples, Duluth, Minn.

this difference is not evident with molybdenum. This behaviour may be the result of beryllium following silicon instead of, or in addition to, aluminium.

Data for tungsten in mafic and ultramafic rocks are lacking, so that comparison with molybdenum as a function of silica content can not be made. In the range 68–78 per cent SiO_2 there is an indication of a slight decrease in the ratio Mo/W with increasing silica. Tungsten seems to show a slight preference for the more silicic rocks. In granitic rocks tungsten is slightly more abundant (on the weight basis) than molybdenum, if the composites analyzed can be considered representative.

We will now consider the distribution of molybdenum in a few series of genetically related rocks.

Michigan Keweenawan. Broderick [33] has studied the differentiation of the basic flows of upper Michigan in detail. The results obtained by him in the examination of the thick (1200 ft) Greenstone basalt flow are of particular interest. This flow has two coarse-grained doleritic zones in its upper half, whose development is thought to be connected with the concentration of hyperfusibles at these horizons. In the lower half of the flow there is a concentration of olivine due to crystal settling. Broderick showed that there is an increase in normative apatite, ilmenite, magnetite, albite, and orthoclase in the doleritic streaks. K, Na, Fe, Mn, Ti, P and Cu are present in these zones in amounts markedly higher than the average, whereas Mg and Al are below average; Si is slightly higher than the average.

Molybdenum has been determined in these samples (Table 9). When the results are plotted in the type of diagram used by Broderick, the concentration of molybdenum in the doleritic zone is clearly shown (figure nor reproduced here). Moreover, samples from the lower portion of the flow (3150–3154), enriched in early crystallizing minerals, are lower than the average in molybdenum. Molybdenum thus follows the elements listed above, and not magnesium.

In Fig. 2, molybdenum is plotted versus TiO_2 for the Greenstone flow, the Kearsarge flow and 10 miscellaneous basic flow rocks of upper Michigan, all described by Broderick. There is an undoubted correlation between the two elements. Experimental error no doubt adds to the scatter of the points. The different flows are indistinguishable in the plot and a common magma source is indicated. In the sub-crystal differentiation producing the lavas of the different flows, molybdenum has followed titanium to a large extent.

A plot of Mo versus $Na_2O + K_2O + TiO_2$ gives a less satisfactory correlation than Mo vs. TiO_2 for the flow rocks as a whole, although the Greenstone and Kearsarge samples give a somewhat better linear relation by the former plot.

The molybdenum contents of the three phases of the Mt. Bohemia gabbro intrusive (gabbro aplite, intermediate gabbro, and basic gabbro as named by Broderick) are also plotted in Fig. 2. The intermediate gabbro occupies a position in the diagram in accord with the flow rocks, but the aplite and the basic gabbro show a different trend, molybdenum no longer rising with titanium. Instead, molybdenum mounts with SiO_2 (45·4, 48·4 and 61·4% for the three rocks). Differentiation in the intrusive thus leads to a different distribution of molybdenum than does differentiation in the flows. It may be noted that TiO_2 tends to rise with SiO_2 in the flows, whereas the relation is reversed in the gabbro series. Determination

of molybdenum in the separated minerals of the rocks may throw some light on the causes of the varying behaviour. No simple relation is evident between the alkalies and molybdenum in the gabbro series. Although Na_2O increases in the

Table 9. *Molybdenum in Keweenawan rocks of Michigan*

Broderick's No.	Mo, *p.p.m.*	*Broderick's No.*		Mo, *p.p.m.*
KEARSARGE FLOW		*MISCELLANEOUS KEWEENAWAN SAMPLES*		
3112	0·9			
3113	0·9	3091	Melaphyre	0·2
3115	0·5	3095	Ophite	0·3
3117	0·2	3103	Glomeroporphyrite	0·3
3119	0·5	3104	Melaphyre	1·2
3121	0·7	3106	Melaphyre	0·5
3123	0·6	3110	Glomeroporphyrite	0·5
Weighted composite	0·5	3127	Melaphyre	0·8
		3129	Melaphyre	0·6
GREENSTONE FLOW		3156	Felsite (intrusive)	1·1
3132	0·2	3157	Felsite	1·4
3134	0·5	3159	Felsite	0·8
3136	1·2	3161	Gabbro, aplite	1·4
3138	0·6	3163	Gabbro, intermediate	0·8
3140	1·7	3166	Gabbro, basic	0·3
3142	0·6	3169	Felsite porphyrite	0·9
3144	0·5	3170	Porphyrite	0·8
3146	0·5			
3148	0·2			
3150	0·1			
3152	0·3			
3154	0·3			
Weighted composite	0·6			

Table 10. *Molybdenum in diabasic and red rock facies of the Endion sill*

Sample	SiO_2 %	Na_2O %	K_2O %	TiO_2 %	Mo *p.p.m.*
Ophitic diabase (No. 1)	47·3	2·5	0·8	2·9	1·7
Diabase at first gradation to red rock (No. 3)	52·4	3·0	2·4	2·7	2·8
Intermediate red rock (No. 4)	61·5	3·3	4·3	1·4	3·3
Red rock within a few feet of rhyolite contact (No. 6)	61·1	3·4	4·1	1·4	2·9
Rhyolite (No. 7)	75·5	3·3	5·2	0·2	1·5

order that SiO_2 increases (2·15, 2·76 and 3·67%) the respective K_2O contents are 3·15, 2·4 and 4·5% for basic gabbro, intermediate gabbro, and aplite.

The felsites of Baro Hill and Mt. Houghton (1·1, 1·4 and 0·8 p.p.m. Mo) are richer on the average than the basic flow rocks in molybdenum, but the difference is not very striking.

Endion Sill; Duluth Gabbro. Schwartz and Sandberg [34] have studied several Keweenawan sills intrusive into basalt and rhyolite flows overlying the gabbro mass at Duluth, Minnesota. These sills show a gradation from diabase

below to silicic "red rock" (granophyre) above. The Endion sill is typical. We have determined molybdenum in four rocks of the Endion sill and also in the rhyolite forming the roof of the sill (Table 10).

Enrichment of the molybdenum in the red rock facies is evident and is in agreement with the hypothesis of SCHWARTZ and SANDBERG that differentiation of the sill magma is primarily responsible for the two facies. The marked difference in molybdenum contents between the overlying rhyolite and the adjacent red rock is to be noted.

The concentration of molybdenum in the red rock phase of the main mass of the Duluth gabbro is even more pronounced than in the red rock of the Endion sill. The gabbro contains 0·4–1 p.p.m. of molybdenum (Table 6), whereas three samples of red rock were found to contain from 2·5 to 4·3 p.p.m.:

	p.p.m. Mo
Red rock, 5th St. and 21st Ave. W., Duluth	2·5
Red rock, 1st St. N. and about 12th Ave. (old quarry). This specimen contains a larger amount of ferromagnesian minerals than the preceding	3·9
Red rock, unspecified locality, Duluth	4·3

The red rock of the intrusion shows roughly a five-fold concentration of molybdenum compared to the gabbro. The concentration factor is thus greater for the red rock of the gabbro than for the red rock of the Endion sill.

A high molybdenum content is also shown by another sample of the red rock facies of the Duluth gabbro from Cook Co., Minnesota. This rock, which has been given the field name syenite [45], contains 3·8 p.p.m. Mo. The molybdenum content of its component minerals is listed in Table 8. Approximately one-half of the total molybdenum is accounted for by the strongly magnetic fraction, which makes up about 7 per cent of the rock.

As may be seen from Fig. 3, molybdenum does not rise with titanium in the Endion Sill samples. In this respect, among others, the course of differentiation in the sill differs from that of the basic Michigan flows. Chemical analyses of the samples of the Duluth gabbro and its red rock are not available and nothing can be said about the relationships here.

Granites of the Llano Region, Texas. The genetically related granites of the Llano uplift region of central Texas have been studies petrographically and chemically by GOLDICH [46]. They are regarded as a portion of a rock series representing differentiation through fractional crystallization.

Table 11 gives the molybdenum contents of these rocks, together with data for tungsten and beryllium available from previous work [47], [48]. Molybdenum tends to rise with silica, but the trend is irregular. The discrepant molybdenum values for the Bear Mtn. granite do not seem attributable to analytical errors, and a sporadic distribution of molybdenum in this rock is suspected. Molybdenite occurs in pegmatites associated with the Llano granites and might be found in the granites themselves. The ratios Mo/W and Mo/Be tend to rise with increasing silica.

Molybdenum is less abundant than beryllium in these rocks, but is not greatly different from tungsten in amount.

Table 11. *Granites of the Llano region, Texas*

Sample	SiO_2 %	Mo, *p.p.m.*		W, *p.p.m.*	Mo/W	Be, *p.p.m.*	Mo/Be
		A[a]	B[b]				
Town Mountain (quartz monzonite)	68·2	(0·9) 0·4	0·3 0·3	1·1	0·3	3	0·1
Petrick	71·9	1·7	1·6				
Cassaday	72·1	0·8	0·6	1·5	0·5	4	0·2–
Granite Mountain	73·0	1·4	1·2	1·6	0·8	7	0·2
Llanite (granite porphyry)	75·2	3·8	3·5	2·6	1·4	6	0·6
Bear Mountain	76·8	0·2 0·2	4·0[c]	2·4	(1·7)[d]	8	(0·5)[d]
Petrick aplite	76·7	0·3	0·2				

[a] Analyses by Kuroda.
[b] Analyses by Sandell.
[c] Sandell and Goldich found 4 p.p.m. in 1943 [6].
[d] Based on 4 p.p.m. Mo.

Table 12. *Molybdenum in West Texas rocks*

Rock	Mo, *p.p.m.*	SiO_2 %	Na_2O %	K_2O %	TiO_2 %
Sheep Canyon basalt	1·2	44·3	3·5	2·2	3·6
Sheep Canyon basalt	1·2	45·7	3·4	1·4	3·2
Elephant Mountain basalt	0·9	46·0	4·3	1·0	2·9
Cottonwood Springs basalt	2·3	46·9	3·8	2·3	2·8
Cottonwood Springs basalt	2·5	48·1	4·5	2·4	2·7
Butcherknife Hill basalt	3·2, 3·2	48·5	5·1	2·4	2·5
Buck Hill syenite	6·4, 6·4	61·0	6·0	5·6	0·5
Potato Hill andesite	0·9	61·5	3·8	2·6	1·5
Crossen trachyte	6·2	71·2	3·9	5·1	0·6
Mitchell Mesa rhyolite	0·6	78·8	1·8	6·3	0·2
Pruett Tuff	0·3	69·7	0·8	4·2	0·2
Duff Tuff	0·2	70·6	1·8	5·1	0·2

Except for the llanite and the questionable Bear Mtn. granite, the central Texas granites are comparable to similar rocks of other regions in their molybdenum contents.

West Texas. The rocks examined for molybdenum are from the Buck Hill quadrangle in west central Brewster County. They have been described by Goldich and Elms [49]. The results are summarized in Table 12, together with the rounded percentages of some of the major constituents. The basalts tend to be

higher than the average in molybdenum, probably because of their alkalic affinities. The high molybdenum content of the syenite and trachyte is notable. These rocks contain respectively 11·6 and 9·0 per cent $NA_2O + K_2O$.

Table 13. *Molybdenum in sedimentary rocks*

Sample	Mo, *p.p.m.*	*Sample*	Mo, *p.p.m.*
SHALE AND CLAY		Dolomite, Ellenburger, Texas	0·5
Vanadiferous shale, Paris-Bloomington District, Idaho	87	Dolomite, Ellenburger, Texas	0·5
Vanadiferous shale, same locality as preceding	65	Limestone, Death Valley Region, Calif.	0·1
Calcareous shale (dark gray), Windy Creek area, Alaska	13	Dolomite (Oneota), near Hastings, Minn.	0·2
Calcareous shale, Windy Creek area, Alaska	2·4	Limestone, (Platteville), Minneapolis, Minn. [50, p. 50]	0·3
Calcareous shale, Windy Creek area, Alaska	1·8	Argillaceous limestone, Trenton, N.Y.	0·1
Organic shale, Katella area, Alaska	9·3	Argillaceous limestone, Bureau of Standards sample la	0·2
Cason shale, Searcy Co., Ark.	2·8	Dolomite, Bureau of Standards sample 88	0·1
Shale, Sawyer Quadrangle, N.D.	1·8	Carbonaceous limestone, Greene Co., Pa.	1·2
Shale, red, Aroostook Co., Maine	0·9		
Tasmanite, near Latrobe, Tasmania	4·6	Manganese-iron carbonate concretion, Chamberlain, S.D.	3·0 (acid soluble) 0·1 (acid insoluble)
Shale, Hanover, N. Mex., hornstone phase	0·3		
Shale, Hanover, N. Mex., epidote phase	80		
Shale, Black Hills, S.D.	0·5	*SANDSTONE AND ARKOSE*	
Shale, Black Hills, S.D., silicified	0·3	Sandstone (St. Peter), Minneapolis, Minn.	0·0
Shale, or siltstone, Bad Lands, near Kadoka, S.D.	0·6	Sandstone, Franconia, Minn.	0·7
Shale, Big Hole River Power Dam, Mont.	2·5	Sandstone, Mt. Washington area, N.H.	1·5
Shale (Dresbach), Interstate Park, Wis.	0·8	Arkose, Pine Co., Minn. [38, p. 91]	1·6
Shale, Interstate Park, Wis., green	0·3	Arkose, Antarctica	0·5
Shale, Interstate Park, Wis., yellow	0·2	Arkose, Antarctica	0·2
Shale, Interstate Park, Wis.	0·8	*CHERT AND NOVACULITE*	
Shale, Interstate Park, Wis., pyritic phase	5·1	Upper chert, Three Mile Hill Section, West Texas	0·3
Decorah Shale, Goodhue Co., Minn.	0·7	Upper chert, Three Mile Hill Section, West Texas	0·9
Decorah Shale, Goodhue Co., Minn.	0·7	Lower chert, Three Mile Hill Section, West Texas	0·3
Decorah Shale, Twin City Brick Co., St. Paul, Minn. [50, p. 54]	0·6	Upper novaculite, Three Mile Hill Section, West Texas	0·1
Decorah Shale, Twin City Brick Co., St. Paul, Minn.	0·6	Upper novaculite, Three Mile Hill Section, West Texas	0·0
Glacial lake clay, Carlton Co., Minn.	1·3	Lower novaculite, Three Mile Hill Section, West Texas	0·0
Glacial lake clay, Carlton Co., Minn.	1·3	Chert, from Oneota, dolomite, Minnesota	0·0
Residual clay, Redwood Falls, Minn. [40, p. 24]	0·0		
Clay, Cretaceous, Morrison Co., Minn.	0·7	*BAUXITE*	
Clay, Cretaceous, Morrison Co., Minn.	0·9	Haiti, composite of main Acetillar ore body (51)	2·9
Shale, green, Rochester, N.Y.	0·2	Demerara, British Guiana	3·6
Bentonite, Gillete, Wyo.	1·3	Bureau of Standards sample No. 69	15
LIMESTONE AND DOLOMITE		*MISCELLANEOUS*	
Limestone, Ellenburger formation, Texas	0·3	Anthraxolite, Balfour, Ontario	3·5
Limestone, Ellenburger, Texas	0·6	Glauconite, Mason Co., Texas	0·6
Dolomite-limestone, Ellenburger, Texas	0·3		

B. Sedimentary rocks

The data for sedimentary rocks are presented in Table 13. The first 9 shales in the table are samples furnished by the U.S. Geological Survey.

All these samples were fused with sodium carbonate and molybdenum was determined in the filtered leach by the method used for igneous rocks.[1] Samples containing sulphides and organic matter were first roasted at 500°C.

There is an undoubted concentration of molybdenum in carbonaceous shales, in agreement with previous findings. Shales not containing much organic matter or sulphide show an average of about 1 p.p.m. of molybdenum, or approximately the same content as igneous rocks as a whole. Because of the wide variation in shales it is very difficult to arrive at an average figure for the whole group. An average higher than for igneous rocks may be expected because of the generally low amounts in limestones and sandstones and the possibility of appreciable amounts of molybdenum having escaped from magmas and being added to the sea and thence to sediments (the molybdenum content of sea water is negligibly small, 0·5 microgram per litre). However, one would not expect these factors to raise the average in all shales to more than two or three times the igneous rock content.

We have determined molybdenum in three composites of shales prepared by Minami [52] and Noll [53] with the following results (Cu and Zn values from Sugawara and Morita [54], C and S values from Minami [52]):

Composite	*Colour*	C, %	S, %	Mo, *p.p.m.*	Cu, *p.p.m.*	Zn, *p.p.m.*
14 Japanese Paleozoic shales (Minami)	Light gray	—	0·12	0·5	40	100
10 Japanese Mesozoic shales (Minami)	Light gray	—	0·20	2·9	55	100
36 European Paleozoic shales (Noll)	Dark gray	1·9	0·32	4·5	65	130

The means of the three composites differ too much for the average of all to be significant. It is perhaps no coincidence that molybdenum and copper increase together. Quite likely organic matter and sulphur play a role in deciding the variable metal contents.

[1] As a check on the sodium carbonate fusion method when applied to carbonate rocks, a composite of the 5 Ellenburger limestones and dolomites was ignited to destroy any organic matter and molybdenum was determined in the acid solution of the residue. The value of 0·4 p.p.m. Mo was thus obtained, compared to 0·4 p.p.m. from the average of the individual determinations after carbonate fusion.

The pyritic phase of the Dresbach shale from Interstate Park, Wisconsin, contains from 5 to 20 times as much molybdenum as adjacent pyrite-free shale (Table 13). Little, if any, organic matter is present with the pyrite. Doubtless the molybdenum is present in the sulphide. The pyrite content is estimated as about one-third by weight of the shale.

The probable reasons for the concentration of numerous metals in shales rich in organic matter and sulphides have been discussed by GOLDSCHMIDT and others and need not be considered here. Because of its chalcophilic properties in aqueous as well as anhydrous environments, it is not unexpected to find molybdenum in sedimentary pyrite.

The average molybdenum content of 12 limestones and dolomites is 0·4 p.p.m. Despite the uncertainty introduced by the small number of samples, it seems safe to say that carbonate rocks are poorer than shales in molybdenum. The traces of molybdenum found in carbonate rocks, as far as they are not accounted for by organic matter or other "foreign" components, may possibly be explained by the very slight solubility of calcium molybdate, which may thus be expected to have some tendency to be incorporated in the rock. The effect of organic matter in raising the molybdenum content is shown by the dark carbonaceous limestone of Greene Co., Pa., which contains 1·2 p.p.m. Mo.

Since molybdenum does not occur in significant amounts in quartz of igneous rocks, such amounts as are found in sandstones are to be attributed to other components. The very pure St. Peter sandstone contains no detectable molybdenum.

Table 14. *Molybdenum in deep sea deposits*

Sample	*Location*	*Depth(m)*	Mo, *p.p.m.*
Globigerina Ooze	Territory of the Pacific Islands	—	3
Red Clay	15°20′ N 151°28′ E	6095	4
Blue Mud	Suruga Bay, Japan	50–2000	3
Blue Mud	34° 8′ N 143°55′ E	6020	5
Red Clay	44°28′ N 157° 4′ E	5728	3
Red Clay	31°18′ N 154°50′ E	5657	2

Chert is usually low in molybdenum. Bauxite contains appreciable but variable amounts, perhaps reflecting different modes of origin, or differences in the source rocks.

Appreciable amounts of molybdenum are found in deep sea deposits, as shown

by Oana [55] and Kuroda [56]. The results obtained by the latter are given in Table 14. The average of the small number of analyses is 3 p.p.m.

From the values for the shale composites given above and for deep sea sediments in Table 14 it seems probable that the average molybdenum content of all sedimentary material does not exceed 5 p.p.m., and could be considerably less. There appears to be more molybdenum in sediments than can be accounted for by the weathering of igneous rocks, and some contribution from volcanic exhalations and thermal waters may be suspected.

C. Metamorphic rocks

No special attempt has been made to trace the distribution of molybdenum in rocks of this type. A few determinations on miscellaneous specimens follow (p.p.m. Mo):

Slate (Rove), Cook Co., Minn.	0·7
Slate (Rove), Pigeon River, Minn.	0·7
Graywacke, near Virginia, Minn.	0·4
Slate Mt. Washington Area, N.H.	1·7
Slate, New York State (4 samples)	0·6, 0·3, 0·2, 0·2
Quartzite, Mt. Washington area, N.H.	0·6
Quartzite, Dell Rapids, S.D.	0·6
Graphite gneiss, Gifu Prefecture, Japan	0·8

The previously reported values for the granite-gneiss composite (0·5 p.p.m.) and the Morton, Minn., granite-gneiss (0·1 p.p.m.) may be included here.

A preliminary survey of molybdenum in the regionally metamorphosed Thomson formation [57] of eastern Minnesota was made. In the following tabulation the samples are arranged in approximate order of increasing metamorphism, from the slate and graywacke on the northeast to the schist and gneiss to the southwest:

	p.p.m. Mo
Slate, Thomson, Minn.	0·9
Slate-graywacke, near Carlton	0·2
Phyllite, Barnum	1·2
Phyllite, Little Falls	0·2
Schist, Denham	0·3
Schist, near Malmo, Aitkin Co.	0·4
Staurolite schist (matrix), Blanchard's Rapids, Morrison Co.	0·2
Granite-gneiss (McGrath), near Dad's Corner, Aitkin Co.	0·5

If these results justify any conclusion it is that the molybdenum content does not increase with the metamorphic grade. Because of the variable composition of the Thomson formation, study of a greater number of samples will be required for definite conclusions.

IV. Molybdenum in Meteorites

Molybdenum contents of two iron meteorites and fourteen chondrites are recorded in Table 15. In addition, molybdenum was determined in the metal, sulphide and silicate phases of two composites prepared from the chondrites whose total molybdenum contents had been determined.

The iron meteorites, or the metal phase of the chondrites, were dissolved in aqua regia, the solution was evaporated to dryness several times with hydrochloric acid, and the usual photometric method was then applied. The silicate and metal phases of the stony meteorites were separated magnetically. Troilite divides in this separation. It was removed from the silicate fraction by treating the finely ground material with a cold 1 : 1 mixture of 2*N* hydrochloric acid and saturated bromine water for 5–10 minutes. Some of the troilite was separated from the iron phase magnetically. Brief treatment of the metal with hydrochloric acid-bromine was ineffective in removing the remainder. Therefore, the amount of remaining sulphide was found by determining sulphur gravimetrically after dissolving the metal in aqua regia, and a correction was subsequently applied. Some silicate also remains with the metal. Its amount was found by igniting and weighing the washed residue from the aqua regia treatment. Some of the silicate (olivine) is brought into solution by the acid. To allow for this, the weight of the residue was multiplied (somewhat arbitrarily) by 1·5 to give the amount of silicate. The metal fraction contained about 30 per cent silicate on the basis of this method of calculation. FeS content of the metal fractions of Composites I and II was 5 and 3 per cent. The metal content of the metallic fraction was probably obtained to within 10–15 per cent of the true value. Perhaps the proportion of metal was slightly overestimated.

The molybdenum content of the troilite of the chondrites was found by determining molybdenum in the hydrochloric acid-bromine leach of the silicate fraction and relating its amount to the sulphate content as found gravimetrically.

Chondrites are quite uniform in their molybdenum content and its seems probable that the average value of 1·6 (1·55) p.p.m. Mo for the fourteen analyzed is not far from the truth. The silicate phase of chondrites contains 0·6 p.p.m. Mo as an average. This value does not agree with Noddack's average of 2·5 p.p.m. for the silicate phase of meteorites. Our value of 6 p.p.m. Mo for troilite of chondrites is much lower than the Noddack average of 22 p.p.m. (based on 3 specimens, 15, 10, 40 p.p.m.) for troilite of iron meteorites.

The available determinations of molybdenum in iron meteorites agree in magnitude:

	Mo, *p.p.m.*
Canyon Diablo (Noddack)	10
Canyon Diablo (this work)	17
Mukerop (Noddack)	21
Mukerop (Klüver-Goldschmidt, (2))	9
Toluca (Noddack)	15
Coahuila (Klüver-Goldschmidt)	11
Henbury (this work)	10

The average is about 15 p.p.m., possibly higher than the average for the metal phase of chondrites (8 p.p.m.), but the number of samples is too small to establish a real difference, especially when the accuracy of the earlier analytical methods can not be estimated.

The present data make molybdenum more siderophilic than the earlier data, i.e. $(Mo)_{metal}/(Mo)_{silicate} = 8/0{\cdot}6 = 13$, as compared to the Noddack ratio $16{\cdot}6/2{\cdot}5 = 7$. According to the new ratio, molybdenum is more siderophilic than iron, for which the partition coefficient is approximately $90/13 = 7$. However, the distribution of molybdenum and iron between the two phases is sufficiently similar to be in substantial accord with the heats of formation of MoO_2 and FeO, namely 65·7 and 64 kg cal per mole per oxygen atom (cf. Wahl [58], and Brown and Patterson [59]). No attempt has been made in the present work to trace the concentration of molybdenum in the silicate phase as a function of the metal content of stony meteorites.

The value 6 p.p.m. Mo in troilite of chondrites verifies the chalcophilic character of molybdenum, and shows that it is almost as marked as the siderophilic character.[1]

Opinions differ regarding the weighting of silicate, metal, and sulphide phases of meteorites to obtain an average representing meteorites as a whole, or the possible cosmic abundance of an element. If we adopt Urey's suggestion [e.g. 60] that chondrites may represent the average composition of cosmic matter, except for the volatile elements, we obtain the weight ratio $Mo/Si = 1{\cdot}6/(18 \times 10^4) = 9 \times 10^{-5}$ or the atomic ratio 3×10^{-5}. (The average silicon content of the chondrites used was not determined, but was assumed to be the same as the reported average of chondrites, i.e. 18% Si.) Probable limits for the weight ratio Mo/Fe may be given. For the silicate phase of meteorites (as represented by the silicate of chondrites) we have $0{\cdot}6/(1{\cdot}3 \times 10^5) = 5 \times 10^{-6}$ for this ratio. For iron meteorites or the metal phase of chondrites the maximum molybdenum content is taken to be 15 p.p.m. so that the maximum value of Mo/Fe for these is $15/(9 \times 10^5) = 1{\cdot}7 \times 10^{-5}$, which may as well be rounded off to 2×10^{-5}. The average ratio should lie between these limits, probably closer to 5×10^{-6}.

The silicate phase of chondrites is apparently somewhat lower than the average mafic rock in molybdenum, and equal to, or somewhat higher than, ultramafic rocks, but the correspondence is very close in either case.

Molybdenum (atomic number 42) is more abundant than its neighbour niobium (atomic number 41) in meteorites as a whole according to the present meteoritic abundance values, namely 0·5 p.p.m. Nb in silicate meteorites and 0·2 p.p.m. in irons [61].

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[1] More marked if the comparison is based on the mole fraction of Fe in the metal phase and of S in the sulphide phase.

Table 15. *Molybdenum in meteorites*

Meteorite	Mo, *p.p.m.*	*Meteorite*	Mo, *p.p.m.*
IRONS		Morland, Kans.	1·5
Canyon Diablo, Ariz.	17	Silicate phase	0·5
Henbury, Australia	10	Plainview, Texas	2·0
		Silicate phase	0·5
CHONDRITES		Roy, N. Mex.	1·6
Alamogordo, N. Mex.	1·4	Composite I (Arriba, Beenham, Cope, Cotesfield, Morland, Plainview, Roy)	
Arriba, Colo.	1·7		
Beenham, N. Mex.	1·6	Silicate phase	0·7
Cope, Colo.	1·6	Metal phase	7·8
Cotesfield, Neb.	1·3	Sulphide phase	5·9
Estacado, Texas	1·7	Composite II (Alamogordo, Estacado, Gladstone, Gruver, Kingfisher, Ladder Creek, Melrose)	
Silicate phase	0·6		
Metal phase	>6[a]		
Gladstone, N. Mex.	1·5	Silicate phase	0·5
Silicate phase	0·6	Metal phase	8·2
Metal phase	>5[a]	Sulphide phase	5·4
Gruver, Texas	1·6		
Kingfisher, Okla.	1·2	*TEKTITE*	
Ladder Creek, Kans.	1·4	Muldoon, Texas	0·5
Melrose, N. Mex.	1·6		

[a] Minimum value; correction not applied for silicate in the metal fraction.

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Book review

Nonradiogenic Isotopes in Geology: A Review, by Earl Ingerson. *Bulletin of the Geological Society of America* Vol. **64,** No. 3, pp. 301–373, 6 figs., 1953. Price $1.50.

In 1950, a committee was appointed in the United States of America by the Division of Geology and Geography (now called the Division of Earth Sciences) of the National Research Council to look into the feasibility of publishing summaries of geologic research, important results, and outstanding contributions. This committee was duly organized as "Committee on Review Articles, Division of Geology and Geography, National Research Council." In cooperation with the Geological Society of America, the Committee, in March, 1953, sponsored the publication, in the *Bulletin of the Geological Society of America*, of the first results of this valuable innovation, viz., three review articles covering various branches in geology. Dr. Ingerson's paper on isotope geology is one of these reviews.

Isotope geology, or nuclide geology, or nuclear geology, to wit, the application of nuclide research to the investigation of geologic phenomena, embodies some of the newest ways and means toward making geology an exact science. Progress in nuclear physics and development of new tools for isotope research have brought isotope geology to a state of constant growth and rapid expansion. Realizing that acceleration continues in this field Dr. Ingerson decided, before the subject would become too complex and cluttered with data, to summarize what has been accomplished and to suggest certain paths for research in the near future. In his paper, he gives a fairly complete summary, digested from a bibliography of 267 references, of the significant results obtained in work pertaining to the natural abundance and manner of distribution of nonradiogenic nuclides. He also discusses some ideas, general principles, and cautions that bear on the subject.

Part I of the paper is a summary of results obtained to date. The following elements are dealt with: H, He, Li, B, C, N, O, Ne, A, Si, S, Cl, K, Fe, Cu, Ga, Ge, Br, Rb, U. The treatment, in general, is very adequate. Some pertinent papers, however, are omitted, e.g., the classic papers of Briscoe and his co-workers (Briscoe and Robinson, *J. Chem. Soc.* **127,** p. 696, 1925; Briscoe, Robinson, and Stephenson, *Ibid.*, p. 70, 1926; Briscoe, Robinson, and Smith, *Ibid.*, p. 282, 1927) on the variations in the atomic weight of boron and the mass-spectrometric work of Osberghaus (*Z. Physik* **128,** p. 366, 1950) on the isotopic constitution of boron in salt minerals. Valley and Anderson in 1947 (*J. Amer. Chem. Soc.* **69,** p. 1871), six years after their preliminary note quoted by Ingerson was printed, published a detailed report on the isotopic constitution of terrestrial and meteoritic iron. On p. 315, Ingerson refers the results and conclusions of Parravano and Pesce (*Atti X:0 Congr. Intern. Chim., Roma,* **II,** p. 401, 1938) to Teis who quoted them in his paper. Many author names are misspelled. Thus, B. F. Murphey and E. A. Gulbransen of oxygen- and carbon-isotope fame and I. Perlman, the nuclear physicist, probably should do well to change their names to Murphy, Gulbranson, and Pearlman, respectively, to comply with the many American writers quoting their papers. Sometimes it is advantageous not to have a secretary! But I will not dwell on such minor flaws in an otherwise very satisfactory treatment.

In Part II, Ingerson discusses a great number of typical current and future problems in isotope geology. Here he mentions probable natural isotope-separation processes and the types of geologic situations in which they may be operative. Also, he suggests typical specific problems for which positive solutions may be expected to be found. Finally, he suggests a number of isotope pairs for which theory indicates a possible measurable natural fractionation. This part is a veritable mine of new ideas for a worker in the field. The reader of the review will certainly conclude with Dr. Ingerson that more and more new fields are bound to open rapidly for this new approach to geologic and related problems. Dr. Ingerson's paper is recommended to all those desiring to obtain up-to-date information about isotope geology. His review certainly also meets the standards set up for good review articles by the Committee on Review Articles in being a comprehensive survey of pertinent literature and embodying critical analysis and constructive synthesis of relevant data.

Kalervo Rankama

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